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Origin and nature of the mineralizing fluids of thrust zone fluorites in Çelikhan (Adiyaman, Eastern Turkey): A geochemical approach

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The Çelikhan fluorite mineralization is concentrated in the thrust zone between the Pınarbası Formation, which forms the hanging wall, and the Kalecik Limestone foot wall. Fluorite occurs as fracture fills in the thrust zone and as replacement of the foot wall. The wall rock alteration consists of calcite, barite, quartz and kaolinite.

The total REE contents of the country rocks, especially the mica- and calc-schists of the Pinarbasi formation at 519 ppm, are higher than those of fluorites. The chondrite normalized REE patterns of country rock and fluorites display generally identical trends. However, fluorite patterns show positive Eu and negative Ce anomaly indicative of low temperature and high fo_2 conditions. Cross plots of the Tb/Ca – Tb/La, $(La/Yb)_n$ – $(Tb/Yb)_n$ and $(La/Yb)_n$ $(Eu/Eu^*)_n$ ratios of the fluorites indicate deposition by low temperature hydrothermal waters. The REE and F were probably leached from the Pinarbasi Formation by the mineralizing solutions. The mineralizing fluids are probably meteoric and formation waters heated at depth along the thrust zone by the natural thermal gradient and/or formation waters heated and mobilized by thrusting.

Keywords: fluorite, rare earth element, mineralizations, thrust zone, Turkey

INTRODUCTION

Fluorite is present in a diverse group of mineral deposits ranging from epithermal to high temperature and high salinity magmatic deposits in varied host lithologies. Because of its distinct geochemical pattern, fluorite rare earth element geochemistry has been used as an aid to investigating fluorite genesis (Schneider *et al*., 1975; Möller *et al*., 1976; Richardson and Holland, 1979; Möller and Morteani, 1983; Strong *et al*., 1984; Ekambaram *et al*., 1986; Constantopoulos, 1988; Eppinger, 1988; Eppinger and Closs, 1990; Subias and Fernandez-Nieto, 1995; Hill *et al*., 2000; Williams-Jones *et al*., 2000; Andrade *et al*., 1999; Bühn *et al*., 2002; Bosze and Rakovan, 2002; Monecke *et al*., 2002) and a similar approach is used in this study.

Fluorite occurs in many Turkish mineral deposits either as a main or accessory constituent (Sagiroglu, 1982; Ozüs and Yaman, 1986; Ozgenc, 1993; Ayan and Ozgenc, 1995; Sasmaz and Celebi, 1999; Sasmaz *et al*., 1999; Koc *et al*., 2003; Sasmaz *et al*., 2005). However, fluorite-bearing mineral deposits are generally high temperature–high salinity magmatic and magmatic hydrothermal deposits (Sagiroglu, 1984; Ozgenc, 1993; Ayan and Ozgenc, 1995; Uçurum *et al*., 1997). The Çelikhan fluorite deposits in this study are unique among Turkish fluorite deposits because of their occurrence in thrust zones and the absence of any magmatic association.

GEOLOGY

The Çelikhan fluorite deposits are located 10 km north of the Çelikhan Township in Adıyaman, Eastern Turkey (Figs. 1 and 2). The Çelikhan area is situated in the Eastern Taurid Belt which is controlled by two major tectonic elements (Fig. 1): the South Eastern Thrust Zone (SETZ) and East Anatolian Fault Zone (EAFZ) (Yazgan and Chessex, 1991; Yigitbas and Yilmaz; 1996). The thrust zone is composed of imbricated blocks bordered by north-dipping low-angle faults (Aktas and Robertson, 1984). The fluorite bearing thrust zone is one of many north dipping thrust fault formed as a result of the collision of the Arabian Plate and Anatolian Plates after the closure of the southern extension of Neo-Tethys. Thrusting in the Celikhan region ended shortly after the formation of the EAF (Late Miocene) (Fig. 1; Sengör and Yilmaz, 1981; Yazgan and Chessex, 1991; Yigitbas and Yilmaz, 1996). Thus, the mineralization cannot be younger than Late Miocene in age. However, thrusting has continued in the region between the EAFZ and the Arabian Plate forming

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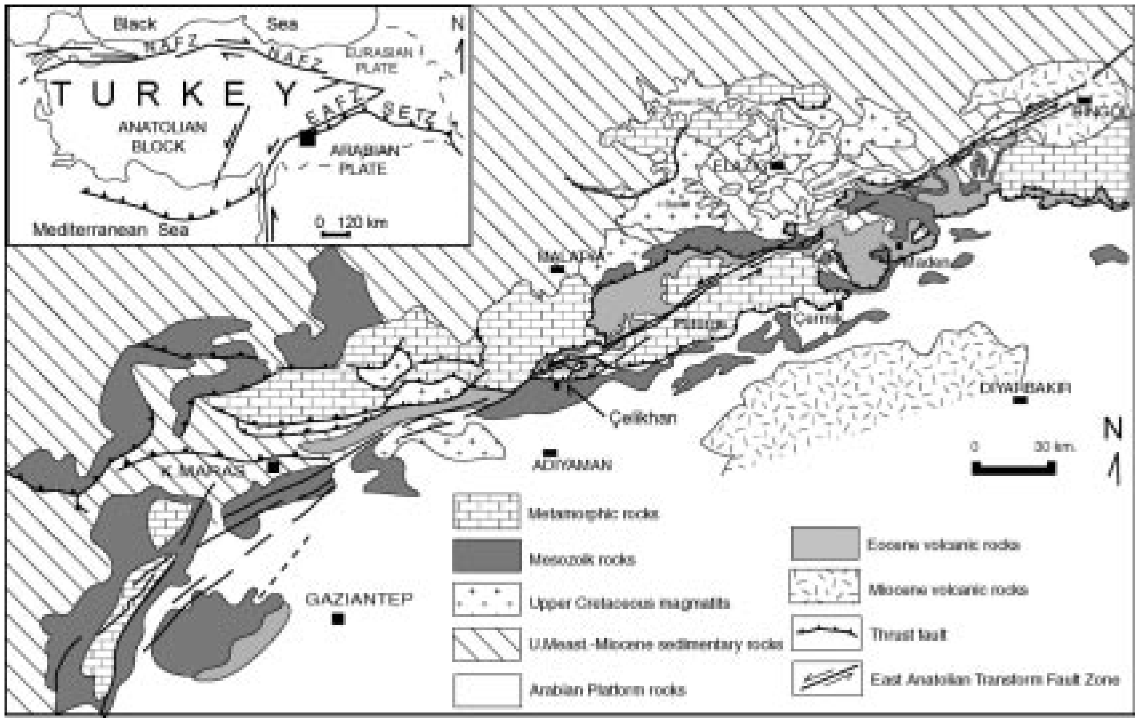

Fig. 1. Simplified geological map of the area between Kahramanmaras and Bingöl, in the South East Anatolian Thrust Zone (Modified from Yazgan and Chessex, 1991) EAFZ: East Anatolian Fault Zone; NAFZ: North Anatolian Fault Zone; SETZ: South East Anatolian Thrust Zone.

thrust zones hundreds of kilometers long (Fig. 1).

These fault zones generally host various mineralization, the most common of which are Cu-sulphide and pyrite. The EAFZ is interpreted as a transform fault system, by many regional geological studies (Piskin, 1972; Gözübol and Onal, 1986; Yazgan and Chessex, 1991; Yigitbas and Yilmaz, 1996), marking the collision of the Anatolian and Arabian plates. The EAFZ itself does not host significant mineralization although its antithetic and synthetic fault zones do host epithermal mineralization such as marcasite and hematite, whose weathered parts provide a source of iron ore.

The Çelikhan fluorite mineralization is hosted by Permo-Carboniferious Malatya metamorphites which covers vast areas south and southwest of Malatya township (Fig. 2). The metamorphites include; marble, limestone, dolomitic limestone, mica-schist and calc-schist, and show features indicative of low pressure and low temperature metamorphism (Gözübol and Onal, 1986). In the study area, the metamorphites are divided into four lithological units. From bottom to top these include mica- and calc-schists of the Pınarbası Formation, stratified and cherty Koltik Limestone, phyllites of the Düzagaç Formation and dolomitic Kalecik Limestone (Fig. 2) (Gözübol and Onal, 1986). No plutonic rocks or evidence of magmatic activity is present in the study area. The nearest evidence for magmatic activity is a small Neogene volcanic body located about 15 kms north of the study area.

FLUORITE MINERALIZATION

The Çelikhan fluorite deposits are concentrated in the thrust zone between the hanging wall Pınarbasi Formation and footwall Kalecik Limestone. Fluorite ore bodies outcrop at Degirmenbasi, Kuz Tepe, Asagiköy and Dalavihami Tepe (see Figs. 2 and 3). Fluorite mineralization within of these four areas have similar features. For example, the fluorite bodies fill fractures in the thrust zone or form replacement pockets and disseminations in the Kalecik Limestone footwall. Here, the fluorite ranges in colour from colourless, to light violet, to violet. Mineralized sections are up to 5 m thick. Flourite and gangue minerals do not exhibit any sign of tectonic deformation. Both the hanging wall and footwall adjacent to the mineralized zones are weakly altered to quartz, carbonate minerals, barite and kaolinite.

The petrographic studies show that the fluorite mineralization and associated wall rock alteration are in response to a single hydrothermal event, and that there is no genetic difference between them.

Many thrust zones are present in the study area al-

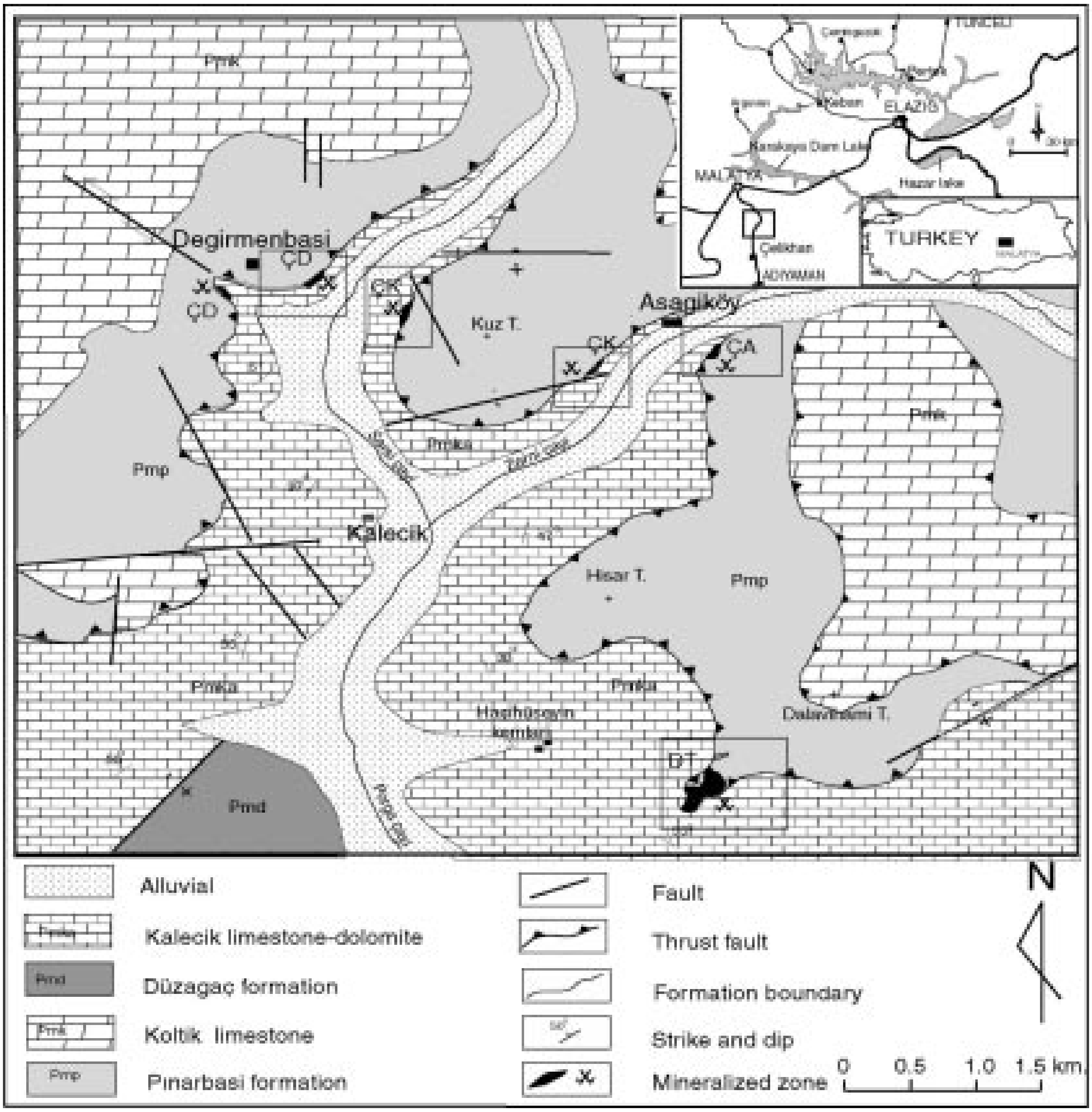

Fig. 2. Location and geological map of the study area (simplified after Gözübol and Önal, 1986). CD, CK, DT and CA are fluorite deposits sectors and sample locations in the study area.

though, only the thrust zone between the Pinarbasi Formation and Kalecik Limestone is host to fluorite deposits (Figs. 2 and 3) suggesting a genetic relationship between the country rock and the deposits. This same thrust zone also hosts Pb-Zn mineralization in the same country rocks as the fluorite mineralization, only further to the west.

GEOCHEMISTRY

Fifteen fluorite samples collected from massive ores in the four areas mentioned above and six samples of country rock were analysed for their major oxide, trace- and rare earth elements by Acme Analytical Laboratories in Canada (Table 1) by ICP-MS, and F by ICP-AES.

REE geochemistry

The total REE contents of Çelikhan fluorites vary within a narrow range from 10 to 42 ppm ($\bar{x}$ = 18 ± 10) as shown in Table 1. The total REE contents of the country rocks vary from 25 ppm in phyllite dominant Düzagaç Formation and Koltik Limestone (Pmk in Table 1), to 68 ppm in the Kalecik Limestone (Pmka), to as high as 519 ppm in the Pinarbasi Formation (Pmp in Table 1). The chondrodite-normalized REE patterns of fluorites and country rocks display similar trends that can be interpreted to imply a genetic association (Fig. 4). Another striking feature of the chondrite-normalized patterns is that the Pinarbasi Formation has higher REE contents than those of the fluorite and other country rocks. REE rich miner-

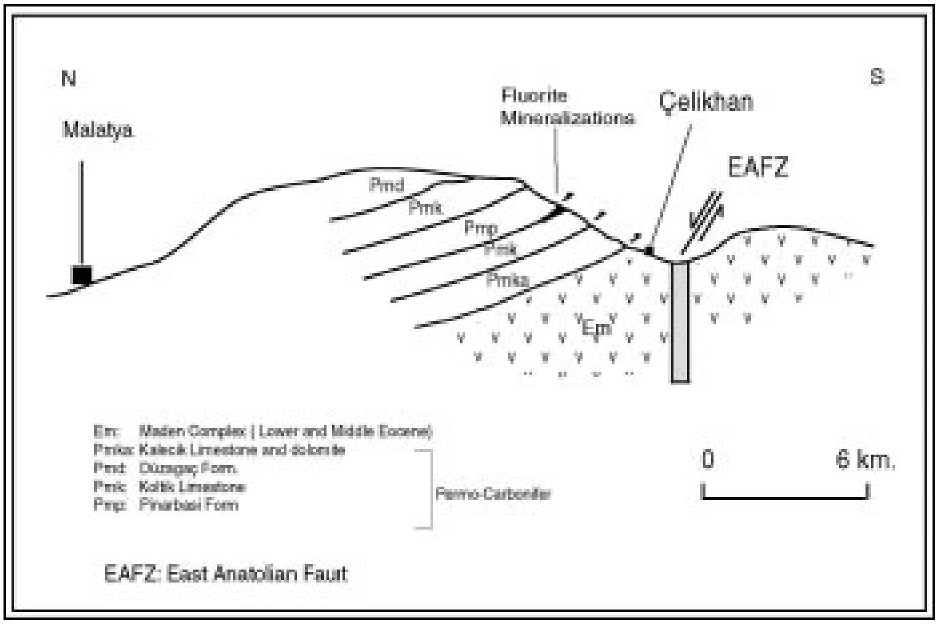

Fig. 3. Cross section showing main structural elements in the study area (modified after Onal and Gözübol, 1992).

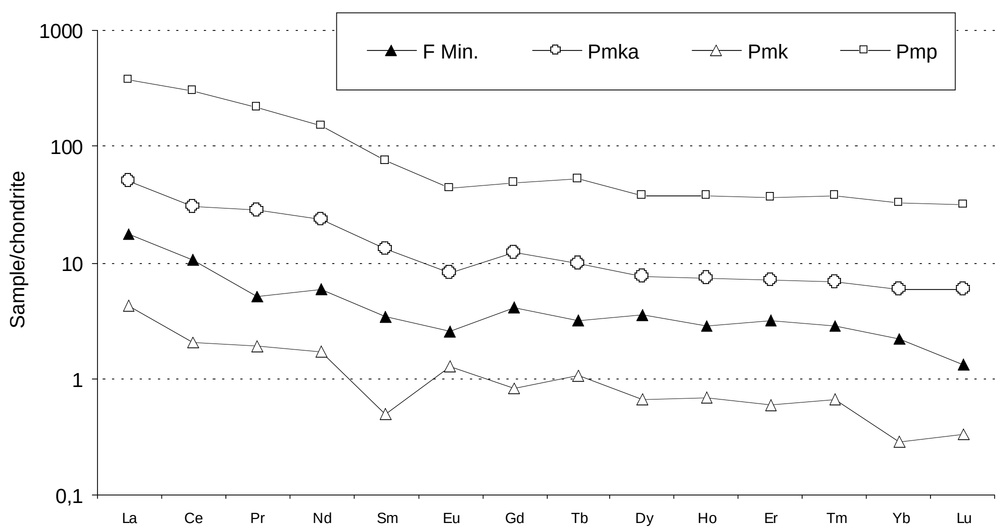

Fig. 4. Chondrite-normalized (Boynton, 1984) REE patterns of the Çelikhan fluorites and country rocks. F min: Çelikhan fluorites, Pmka: Kalecik limestone-dolomite, Pmk: Koltik limestone, Pmp: Pinarbasi formations.

als such as monazite and xenotime are not observed in the schists of Pinarbasi Formation and it is not possible to determine the REE rich minerals of the schists. Çelikhan fluorites also contain anomalous Au contents ranging from 84 to 575 ppb.

In a Tb/Ca versus Tb/La diagram (Fig. 5), Çelikhan fluorites plot in the hydrothermal field (Möller *et al.*, 1976). The fluorites also plot within the low Tb-low La field in the $(La/Yb)_n$ – $(Tb/Yb)_n$ diagram (Fig. 6) which includes many other hydrothermal deposits, such as Akdagmadeni (Sasmaz *et al.*, 2005) and New Mexico (Hill *et al.*, 2000). In a $(La/Yb)_n$ – $(Eu/Eu^*)_n$ diagram the fluorites plot in the same region as vein-type Tad D., Hensen and Chise district barren fluorites veins and Truth Ba-Pb veins. These are all low-temperature hydrothermal deposits (Fig. 7). The same diagram also shows HREE enrichment and positive Eu anomaly in relation to chondrite trends (Fig. 7). This same trend is also observed

Table 1. Major oxide, minor and trace element contents of Çelikhan fluorites and average of country rocks. Refer to Fig. 4 for abbreviation of country rocks. CD, CK, DT and CA are fluorite deposits sectors and sample locations.

Sample No.	ÇK2	ÇK3	ÇA3	ÇD2	ÇD3	ÇD5	ÇD6	DT1	DT2	DT3	DT7	DT8	DT9	DT10	DT11	Pmka	Pmk	Pmp
%																		
SiO_2	13.4	3.3	11.4	52	8.1	58.7	62.8	29.8	28.4	31.8	12.08	19.17	43.41	39.48	25.83	23.67	4.86	77.6
Al_2O_3	0.8	0.25	0.45	1.3	0.35	0.44	0.46	1.4	1.8	1.7	0.12	0.33	0.37	0.38	0.33	3.92	0.13	11.5
Fe_2O_3	0.26	0.2	0.18	0.2	0.25	0.62	0.6	32	0.26	0.26	0.4	0.19	0.38	0.38	0.24	1.99	0.52	1.05
MgO	0.07	0.06	0.08	0.07	0.09	0.02	0.02	0.08	0.08	0.07	0.02	0.03	0.02	0.02	0.03	1.14	1.31	0.71
Na_2O	0.12	0.14	0.14	0.12	0.14	0.01	0.01	0.11	0.1	0.07	0.01	0.03	0.05	0.01	0.01	0.24	0.05	0.26
K_2O	0.3	0.11	0.15	0.29	0.12	0.04	0.04	0.27	0.31	0.21	0.04	0.04	0.04	0.04	0.11	1.06	0.07	6.61
TiO_2	0.05	0.01	0.02	0.05	0.02	0.06	0.03	0.05	0.06	0.05	0.04	0.02	0.05	0.03	0.04	0.22	0.01	0.12
Ca	54	55	54	27	59	16.1	15.9	45	44	49	44.7	37.6	23.8	26.2	32.5	36.31	50.7	0.5
F	33	37.4	37.4	19.8	39.6	21.4	18.4	28.6	30.8	26.4	37.7	39.8	28.6	30.6	36.7	0.066	0.003	0.068
ppm																		
Ba	29455	71591	289	27	18	11	18	25	19	17	23	39	37	38	19	88	9	764
As	310	120	33	75	40	67	65	87	80	71	370	72	297	175	58	3.7	1.3	1.2
Ni	—	—	—	24	20	4	29	—	—	—	2	1	2	3	2	5	2.5	8
Sr	408	1122	85	65	49	84	65	52	56	46	26	24	18	19	21	736	1318	136
Zr	24	91	24	21	14	12.2	11.9	—	105	20	8.2	5.5	8.5	8.4	5.8	41	2.7	292
Sb	8.4	3.1	2.1	12	7.3	9.8	8.6	18	16	15	28.8	4.5	192	139	8.5	0.1	0.2	0.1
Th	4.5	3.5	1.9	1	1.8	1.6	1.5	2	2.5	2.2	3.5	2.3	2	1.9	2.2	3.8	0.1	27
U	—	—	0.9	5	1.5	4.5	4.4	3.4	3.1	4.6	1.7	2.2	5.8	4.7	2.4	1.7	1.3	5.3
Zn	54	470	102	62	428	10	17	94	60	119	8	24	71	48	24	29	5	12
Sc	0.7	0.3	0.3	0.5	0.3	0.6	1	0.7	0.8	0.7	0.6	0.5	0.8	0.7	0.8	4	1	4
La	4.8	1.9	6.4	8.6	4.7	8	6	12	12	9	2.1	1	1.6	1.2	1.2	15.5	1.3	116
Ce	7	5	10	11	5	11.3	8.4	12	16	10	3.9	2	2.8	2.3	2.3	22.3	1.5	223
Pr	0.49	0.3	0.25	0.41	0.56	1.35	0.98	0.88	1.05	0.73	0.48	0.38	0.43	0.37	0.39	3.41	0.23	26
Nd	3	2	4	3	4	4.7	3.7	3	7	11	2.3	2.2	1.9	1.9	2	13.6	1	91.4
Sm	0.6	0.6	0.8	0.5	0.9	0.6	0.5	1.0	1.0	0.9	0.6	0.6	0.4	0.5	0.5	2.6	0.1	15.2
Eu	0.15	0.20	0.20	0.20	0.30	0.08	0.09	0.30	0.20	0.30	0.13	0.14	0.11	0.12	0.12	0.58	0.09	0.31
Gd	1.39	1.53	0.96	1.08	1.4	0.43	0.39	1.25	1.94	1.35	0.86	0.99	0.72	0.82	0.82	3.16	0.22	12.6
Tb	0.16	0.29	0.14	0.15	0.16	0.07	0.07	0.15	0.15	0.12	0.12	0.15	0.11	0.13	0.13	0.54	0.05	2.44
Dy	1.26	1.57	1.4	1.18	1.2	0.5	0.52	0.86	1.11	0.95	0.83	1.17	0.86	0.96	0.96	2.51	0.22	12.6
Ho	0.18	0.26	0.14	0.34	0.31	0.11	0.1	0.17	0.27	0.23	0.18	0.25	0.18	0.21	0.21	0.51	0.05	2.65
Er	0.6	0.8	0.8	0.8	0.8	0.3	0.3	0.4	0.8	0.6	0.5	0.7	0.5	0.6	0.6	1.41	0.12	7.7
Tm	0.09	0.14	0.08	0.07	0.1	0.05	0.05	0.06	0.09	0.08	0.05	0.08	0.06	0.08	0.07	0.2	0.05	1.13
Yb	0.46	0.63	0.50	0.30	0.46	0.25	0.23	0.60	0.46	0.38	0.28	0.49	0.35	0.4	0.41	1.3	0.06	6.9
Lu	0.04	0.05	0.04	0.05	0.04	0.02	0.02	0.03	0.04	0.04	0.03	0.05	0.04	0.05	0.04	0.18	0.01	0.95
Σ REE	20.22	15.27	25.71	27.68	19.93	27.76	21.35	32.7	42.11	35.68	12.36	10.2	10.06	9.64	9.75	67.8	5	518.88
ppb																		
Au	172	84	241	355	163	360	322	325	393	470	575	235	395	312	355	1.9	0.7	2

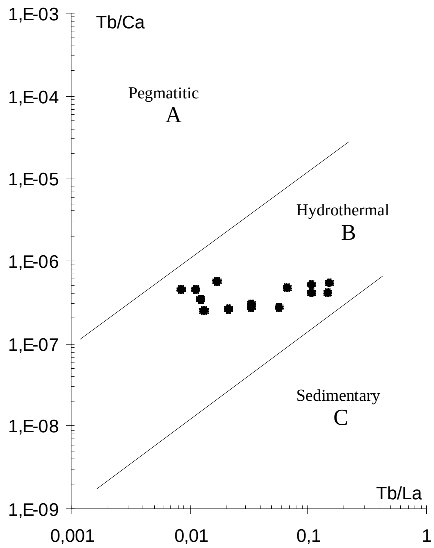

Fig. 5. Plot of Tb/Ca versus Tb/La for Çelikhan fluorites. Trend A shows primary crystallization, trend B represents remobilisation of earlier-formed fluorite, and trend C represents interaction of original hydrothermal F-bearing fluids with limestone wall rocks. Trends are taken from O'Connor et al. (1995).

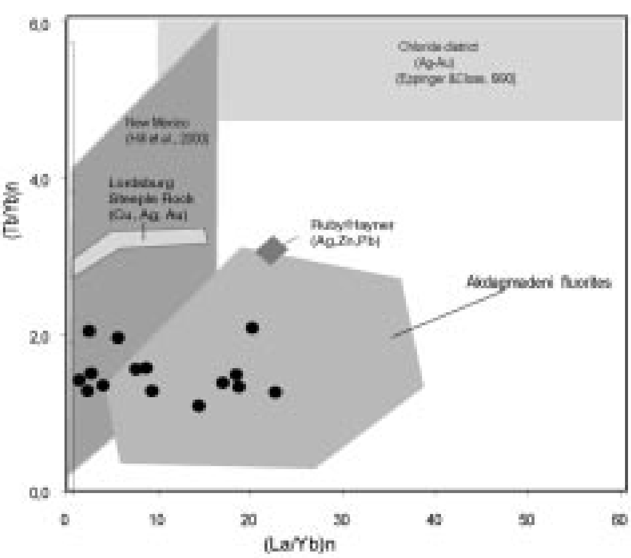

Fig. 6. (Tb/Yb)$_n$ ratio versus (La/Yb)$_n$ ratio of the studied fluorites. All values are normalized to chondritic meteorites, denoted by subscripted "n". Data (Eppinger, 1988) for fluorite associated with precious metals veins in the Chloride district and Akdagmadeni (central Turkey) are also plotted. 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 also plot in the field defined by these Au bearing deposits. The Çelikhan fluorites are characterized by low Tb/Yb and La/Yb ratios.

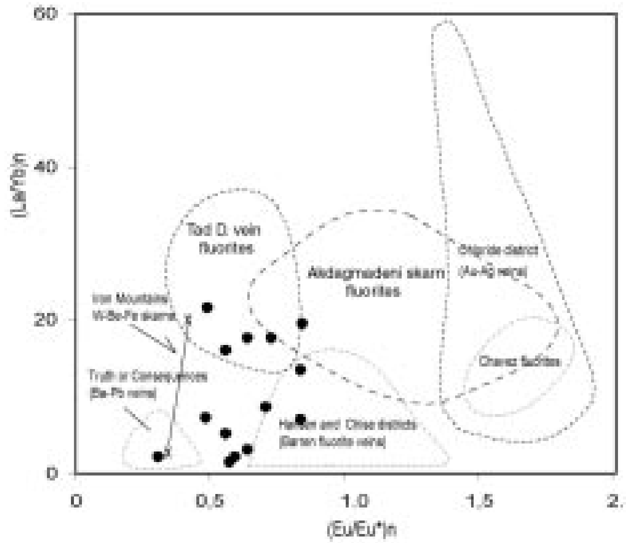

Fig. 7. Chondrite-normalized plot of (La/Yb)$_n$ versus Eu behavior, (Eu/Eu)$_n$.*

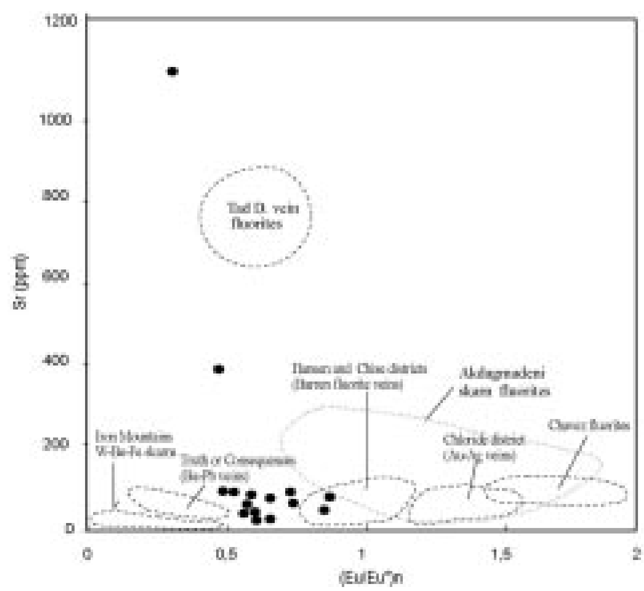

Fig. 8. Sr versus Eu behaviour (Eu/Eu)$_n$ diagram. Due to low Sr contents the fluorites studied here differ from the fluorite deposits described in Hill et al. (2000).*

in a Sr – (Eu/Eu*)$_n$ diagram (Fig. 8). In addition, the Sr contents are very low and may indicate non magmatic origin. The Çelikhan fluorites data coincide with data of Rift and Akdagmadeni fluorites in the Sr – Sc/Eu diagram (Fig. 9). Low Sc/Eu ratios indicate a sedimentary environment. The low ∑REE content is easily seen in Sc – ∑REE diagram (Fig. 10).

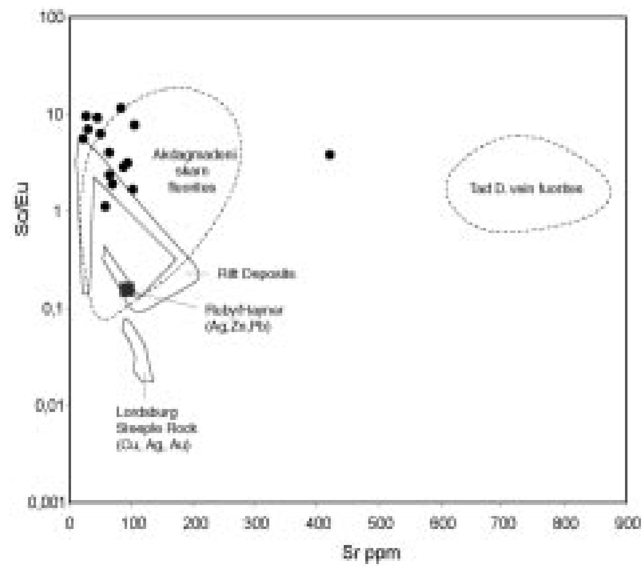

Fig. 9. Sc/Eu ratios versus Sr contents. Note the generally low Sr contents and very high Sc/Eu ratios of the Çelikhan fluorites.

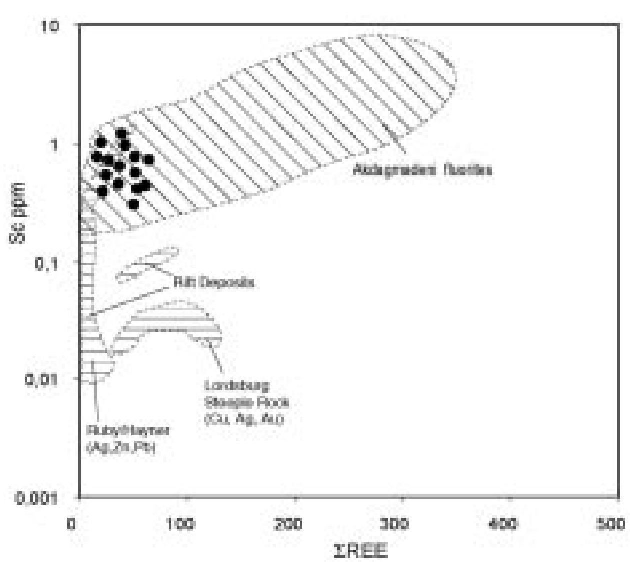

Fig. 10. Sc versus the sum of analysed REE (ppm). Pluton-hosted fluorites tend to have the highest total REE abundance (Sasmaz et al., 2004). By contrast, the Çelikhan fluorites have some of the lowest values.

DISCUSSION

The occurrence of Çelikhan fluorites in fracture fills in the SETZ and as replacement of the footwall, where it is associated with weak wall rock alteration support an epigenetic origin for this mineralization.

The total REE content of Çelikhan fluorite is very low and varies within narrow intervals from 10 to 42 ppm ($\bar{x}$ =18 ± 10). The fluorites with low total REE are interpreted to be derived from a sedimentary environment (Ronchi *et al*., 1993; Hill *et al*., 2000).

Similar chondrite normalized REE patterns for the fluorites and the country rocks indicate a genetic relationship. However, the fluorites exhibit a positive Eu anomaly but a small negative Ce, indicative of low temperatures and high fo_2 conditions. Workable fluid inclusions are not present in the fluorite or quartz and thus it was not possible to confirm the formation conditions indicated by the geochemical data. Plots of Tb/Ca versus Tb/La $(La/Yb)_n$ – $(Tb/Yb)_n$ and $(La/Yb)_n$ – $(Eu/Eu^*)_n$ are consistent with a hydrothermal origin for the mineralizing waters.

The ∑REE and F contents (Table 1) of the Pinarbasi Formation are extraordinarily high at 519 and 680 ppm, respectively, and could be the source for the REE and F of the mineralizing waters. Total REE contents of the fluorites are lower than those of the Pinarbasi Formation due to low mobilities for REE. Fluorine has a higher mobility than REE (Rose *et al*., 1979) and therefore was probably more easily leached by hydrothermal solutions from the Pinarbasi Formation before being deposited in the thrust zone, or as replacement of the limestone.

The source of the mineralizing hydrothermal solution is not clear. Fluorite REE geochemistry does not show a magmatic signature. This is supported by the absence of any evidence for magmatic activity product in the region. The low temperature of the hydrothermal solutions is further supported by the wall rock alteration assemblage. The mineralizing solutions could be circulating meteoric water heated via the natural thermal gradient at depth within the thrust zone, or hot solutions generated during thrusting. There are several examples of heated meteoric water due to thrusting and faulting in the SETZ and EAFZ (Yazgan and Chessex, 1991). Although the surface temperatures of these solutions are low, with a maximum of 48°C at Çermik (Diyarbakir) and 28°C at Ispendere (Malatya; Fig. 1), they contain high concentrations of elements (1,370 ppm) and ions (2,205 ppm) in solution (Cetindag *et al*., 1991; Sahinci, 1991). It would appear that these hydrothermal solutions are formed in a well developed thrust system that cuts several different lithologies of variable geochemical signature. These hydrothermal fluids are expected to form complex mineral assemblages and more voluminous mineralized bodies and alteration zones than simple hydrothermal systems that cross-cut a few lithologies.

The Çelikhan fluorites occur as small ore bodies confined to the SETZ and in the immediate vicinity of the limestone footwall. The mineral assemblage and wall rock alteration mineral suite of the studied mineralization are very weak consisting of fluorite, barite, quartz, kaolinite and carbonates. The ore formed by a thrusting mechanism which had a relatively short strike length and which traversed a small number of lithologies (Figs. 2 and 3). The water was supplied either from meteoric sources or formation waters of the Pinarbasi Formations, or from a combination of both.

CONCLUSIONS

The Çelikhan fluorite mineralizations is one of many examples of thrust zone mineralizations that occur in the SETZ in the eastern Taurid region which contains mineralizations derived from local lithologies cut by the thrusts. Fluorite bodies of Çelikhan occur as thrust zone fillings and footwall replacements along the thrust zone between the Pinarbasi formation and the Kalecik Limestone.

The geology of the area, geochemical data, mineralogy and wall rock alteration all indicate that the Çelikhan fluorites formed under low temperature, high fo_2-hydrothermal conditions with no evidence for magmatic input.

The mineralizing hydrothermal solutions are probably 1) meteoric waters heated by the natural thermal gradient at depth within the thrust zone, or 2) formation waters heated and mobilized by thrust-faulting, and/or 3) a combination of these two.

The simple mineralogy, limited mineralization and weak alteration intensity indicate that whatever the mechanism was, the deposition of fluorite and associated wall rock alteration occurred within a short time interval and by a single hydrothermal event. These conclusions are verified by geochemical data as follows.

Low total REE contents in the fluorites are consistent with a lack of magmatic input. There is no evidence for plutonic bodies or any magmatic input in the Çelikhan fluorite district (Fig. 2). The Pınarbası Formation has the highest ∑REE and F contents and is considered the likely source of REE in the fluorites as it forms the hanging wall to the mineralization. The fluorites display strong positive Eu anomalies (Fig. 4) that indicate low temperatures and high fo_2 conditions during mineralization, as low fo_2 does not allow the conversion of Eu^{+2} to Eu^{+3} which substitutes for Ca^{+2} within the fluorite crystal lattice (Constantopoulos, 1988; Ekambaram *et al.*, 1986; Palmer and Williams-Jones, 1996; Hill *et al.*, 2000; Sasmaz *et al.*, 2004). In general, fluorites associated with precious metal deposits show positive Eu anomalies (Palmer and Williams-Jones, 1996; Hill *et al.*, 2000; Sasmaz *et al.*, 2004). The slightly negative Ce anomaly (Fig. 4) also indicates high oxygen fugacity as Ce^{+3} is oxidized to immobile Ce^{+4} (Constantopoulos, 1988; Palmer and Williams Jones, 1996; Hill *et al.*, 2000).

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