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Fluorite-Barite-Rare Earths Deposits at Kizilcaören, Turkey

Dedicated to Prof. W. E. Petrascheck
on the occasion
of his 80th birthday

By E. F. STUMPFL and M. S. KIRIKOGLU*)

With 5 figures and 2 tables

Abstract

The Kizilcaören F-Ba-Th-REE deposits occur in Tertiary greywackes and pyroclastites. Major components are barite, fluorite, and, to a lesser extent, bastnäsite $Ce[F|CO_3]$; there are also accessory brockite $CaTh[PO_4]_2.H_2O$, florencite $CeAl_3[(OH)_6|(PO_4)_2]$ and monazite ($CePO_4$). Mineralisation is linked to Pliocene alkali volcanism çarbonatite emplacement, and to the late stages of the evolution of the Aegean Rift. Reserves include 0.4 m. t. ore with 0.2% ThO_2 and 4.0 m. t. ore with 3% REE (Ce, La, Nd, Y).

Zusammenfassung

Die F-Ba-Th-SEE Lagerstätten von Kizilcaören sitzen in Tertiären Grauwacken und Pyroklastiten auf. Hauptkomponenten sind Baryt, Flußspat und, in geringeren Mengen, Bastnäsit $Ce[F]CO_3]$; akzessorisch kommen u. a. Brockit $CaTh[PO_4]_2.H_2O$, Florencit $CeAl_3[(OH)_6|(PO_4)_2]$ und Monazit ($CePO_4$) vor. Die Mineralisation ist genetisch an Pliozänen Alkalivulkanismus, der auch Karbonatite gefördert hat und mit der Entwicklung des ägäischen Grabens zusammenhängt, gebunden. Erzreserven umfassen u. a. 0,4 Mio. t mit 0,2% ThO_2 und 4,0 Mio. t mit 3% SEE (Ce, La, Nd, Y).

Introduction

At Kizilcaören in the Eskisehir district, western Anatolia, fluorite-barite-rare earth deposits have been emplaced into a sequence of Tertiary greywackes and pyroclastics (Figs. 1, 2). Trachytes and phonolites occur in the area, and these are related to the development of the Aegean Rift in Tertiary times. In addition to fluorite and barite, which are the main minerals, the veins also carry bastnaesite and florencite, resulting in average concentrations of 3% Ce + La + Nd + Y, and 0.2% Th.

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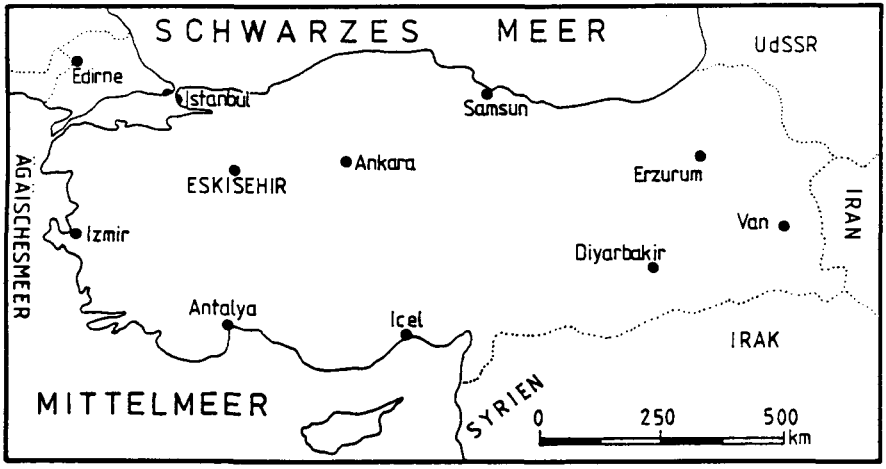

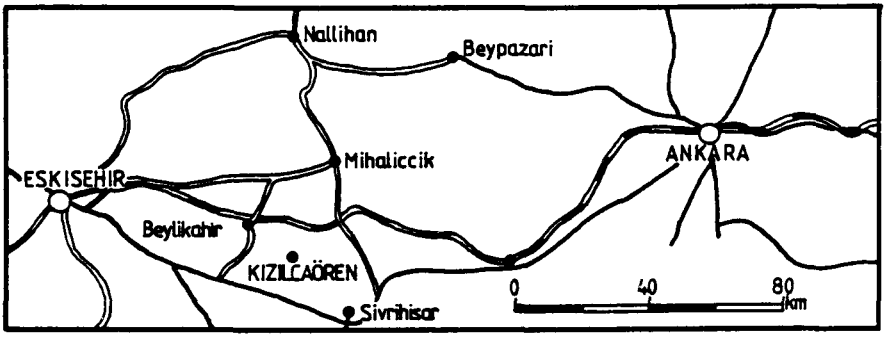

Figs. 1 and 2: Location maps of the Kizilcaören mineral district.

The area forms part of the east-west striking Anatolides, one of Turkey's four main tectonic units. Major rock types in the Sakarya massif of the north-western Anatolides, where Eskisehir is situated, include metamorphics of Upper Paleozoic age, ophiolites emplaced during the Jurassic/Cretaceous, clastic sediments (conglomerates, calcarenites, limestones) of Jurassic-Lower Cretaceous age, and a sequence of Paleocene-Oligocene arenites (KULAKSIZ, 1977). All these are unconformably overlain by the Hoyuklu Formation, consisting of alkaline trachytes, tuffs and pyroclastics, into which the mineralized veins have been emplaced (Fig. 3). Associated phonolites have been dated by DELALOYE & ÖZGENC (1983); they report late Oligocene (Chattien) ages of 22 to 26 m. a.

South of the mineralized area, trachytes and phonolites of Paleogene age cut the Hoyuklu Formation. These rocks form part of the western Anatolian volcanic province, which also includes andesite, trachy-andesites and rhyolites. On the continental scale, Paleogene volcanism is linked to the final stages of the development of the Aegean Rift, which commenced in the Lower Mesozoic and has been attributed to movements of the Arabian Plate towards the Eurasian Plate.

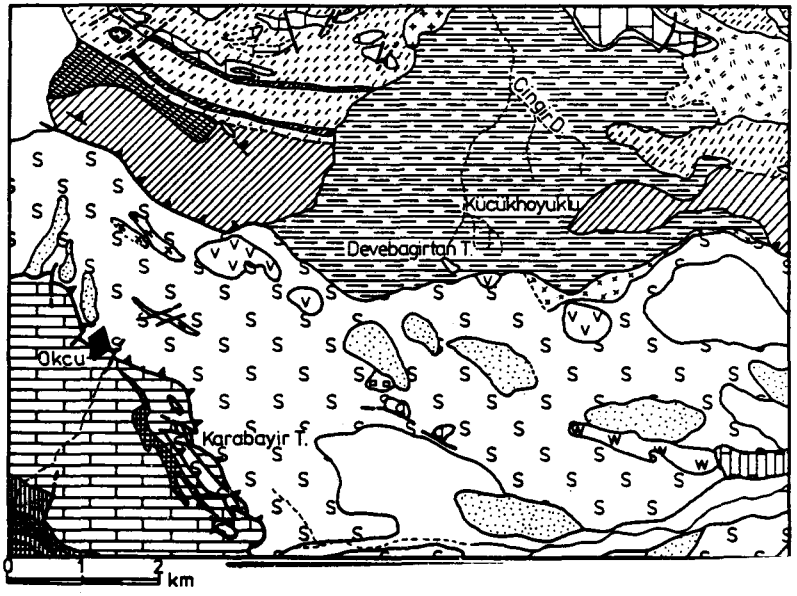

Fig. 3: Geological sketch map of the Kizilcaören mineral district.
Horizontal striations = volcanic Hoyuklu formation, diagonal striations = limestones, s = serpentinites, spots = sand and gravel, white = alluvium. The richest F-Ba-Th-REE veins occur on the slopes of Devebagirtan Tepe (centre of map) at about 1200 m above sea-level.

The Rocks of the Ore Environment

The juxtaposition of mineralization, volcanism and rifting suggests genetic links. All orebodies occur in pyroclastic rocks and in metamorphosed greywackes; special attention was devoted to the investigation of the latter, and to the phonolites and trachytes. The pyroclastites comprise tuffs, volcanic breccias and agglomerates, and cover an area of about 10 km^2. There are glass tuffs, lithic tuffs and crystal tuffs; the latter carry alkali feldspars, albite, quartz, biotite, pyrite and manganese oxides. Representative XRF-analyses of tuffs are given in Table 1; many are of trachytic composition. The occurrence of carbonatites (DELALOYE & ÖZGENC, 1983; KIRIKOGLU, 1983) is considered particularly relevant for understanding the geotectonic position and the Ba-F-REE association of the deposits.

There are two phonolite "pipes" in the southern part of the study area; they form the highest hills approaching 1.300 m in altitude. Trachytes are exposed in three small areas further to the West; they have been emplaced preferentially along the contact between pyroclastites in the north and serpentinites in the south. The phonolites carry up to 15 vol.% mafic components.

Microprobe analyses reveal these to be magnesian hastingsitic hornblende, and aegirine-augite. Representative microprobe analyses of pyroxenes are given in Figure 4. Leucite and noselite are also present; all these occur, together with sanidine, in a fine grained matrix made up of minute grains of these minerals. The

Tab. 1: Representative XRF analyses of tuffs.

Sample No.	SK.28	SK.64	B.1	K.41
SiO_2	48.06	53.90	72.08	60.22
TiO_2	0.22	0.48	0.53	0.14
Al_2O_3	12.94	16.24	13.68	16.10
Fe_2O_3	0.19	0.38	0.10	0.09
FeO	1.10	2.18	0.56	0.52
MnO	0.06	0.29	0.01	0.06
MgO	1.18	1.33	1.41	0.05
CaO	23.50	11.54	0.35	8.46
Na_2O	1.74	0.73	3.95	0.39
K_2O	9.89	12.17	4.70	12.00
Be	23	11	9	9
Sr	1000	146	92	1000
Ba	4000	4000	4800	3000
Li	27	87	54	20
V	80	167	25	80
Cr	15	23	15	7
Co	9	10	8	7
Ni	47	12	8	9
Cu	6	7	8	6
Zn	32	92	13	25
La	110	127	21	184
Ce	186	186	38	161
Nb	21	40	15	38

trachytes typically carry microcline, sanidine, augite and hornblende in a sanidine-rich matrix with well-preserved flow textures.

Chemical analyses support the petrographic identification of the volcanic rocks. The trace element contents of trachytes, phonolites, and tuffs are of particular interest. Representative analyses are shown in Table. 1. Values for barium range from 1000 to 4000 ppm, for cerium from 40 to 700 ppm, for niobium from 20 to 360 ppm, and for lanthanum from 20 to 500 ppm. These are significantly in excess of average values for trachytes and phonolites, and similar to maximum values for nepheline syenites. Of interest is also a thorium value of 329 ppm recorded in a phonolite; all these are considered significant for the interpretation of the derivation of these elements in the associated Ba-F-REE deposits.

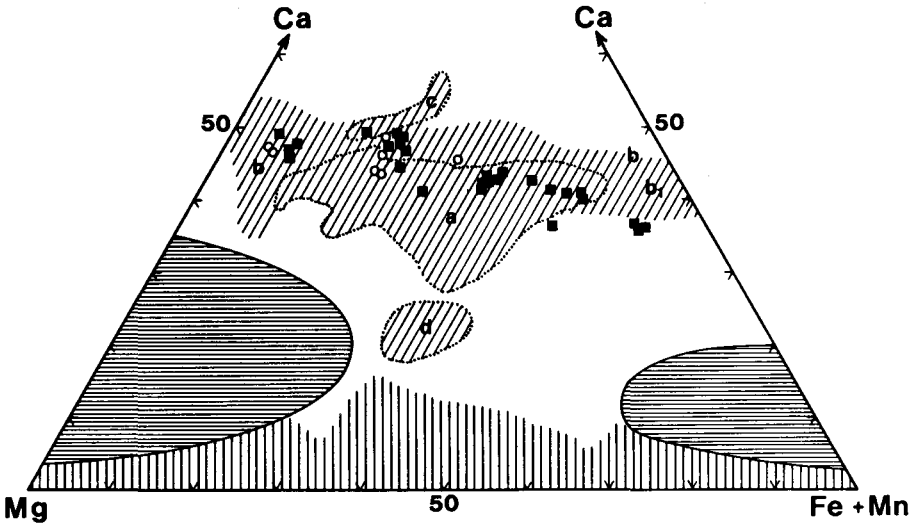

Fig. 4: Microprobe analyses of pyroxenes from volcanic rocks in the Kizilcaören mineral district.
Squares = phonolites, circles = trachytes.
a = augite and aegirine augite; b = diopside-hedenbergite; b_1 = aegirine; c = titanaugite; d = subcalcic augite.

The Orebodies

Mineralization at Kizilcaören was discovered in the late 1950ies by aerial gamma-ray spectrometry; the anomalies then recognized were caused by significant thorium contents in rare earth carbonates. This initial survey was later followed up by stream sediment sampling and drilling in an attempt to determine the thorium potential of the area (KUPFAHL, 1954; KAPLAN, 1977). This and the recent increase in interest in barite and fluorite have prompted a detailed geological investigation of the area, some of the results of which are presented in this note.

Fluorite-barite-Th-REE veins of up to 20 m width have been emplaced into metagreywackes following NW-SE and NE-SW directions. Breccia orebodies also occur in the overlaying pyroclastic rocks preferentially following s-parallel joints. They can be interpreted as products of hydrothermal activity linked to Pliocene alkali volcanism. The largest deposit in the area is Devebagirtan Tepe (Fig. 3), which covers an area of 0.8 km^2; drilling has established continuation of mineralization to depths of 200 m below surface. Other economically significant deposits are Koca Devebagirtan Tepe, Yailabasi and Kücükhoyuklu; there are also several smaller occurrences. Figure 5 is a schematic section showing the stratigraphy and the relative position of orebodies.

There are three structural types of mineralization: coarse-grained vein fillings breccia ores cementing pyroclastic rocks, and lense-shaped stratified orebodies, reaching thicknesses of up to 50 m (Devebargirtan Tepe) in pyroclastic rocks.

The mineralogy of the ores is comparatively simple and does not change with structural style. Major components are fluorite and barite with minor amounts of bastnaesite ($Ce[F|CO_3]$), phlogopite and pyrite, and accessory brockite ($CaTh[PO_4]_2.H_2O$), florencite ($CeAl_3[(OH)_6|(PO_4)_2]$), monazite ($CePO_4$) and quartz, chalcedony, calcite and dolomite. The last four minerals have, so far, not been recognized in hand specimens but only in thin sections. Small amounts of fluocerite (Ce, La, REE)F_3 and strontianite have been identified by X-ray diffraction.

Generally, two main phases of mineralizataion can be distinguished. The first resulted in the formation of coarse-grained (mm- to cm-size) fluorite and barite with

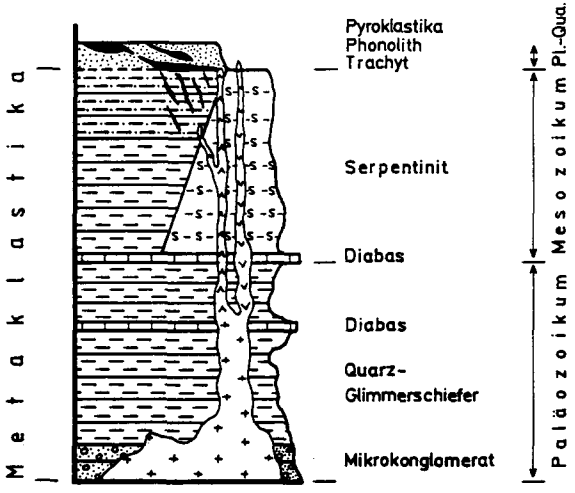

Fig. 5: Generalized section through the Kizilcaören deposits. Total thickness of strata shown is about 4500 m.
+++ = syenitic magma, ∨∨∨ = phonolite, ∧∧∧ = trachyte, black = ore veins.

pyrite and phlogopite. This is particularly well developed in vein-type deposits. The second was responsible for partial brecciation of the first-formed minerals, and for deposition of a matrix consisting of fluorite, barite, phlogopite and REE minerals. Fluorite is the main component of the matrix. It is important to note that REE-minerals can, because of their fine grainsize (less than 0.01 mm) not be identified by optical methods. The diagnosis is based on X-ray diffraction and compositional data obtained with the electron microprobe. Although present in all morphological types of deposits, ores rich in matrix predominate in breccias which preferentially occur in pyroclastites.

Textural evidence supporting the concept of a second generation of mineralization includes brecciation of first-generation minerals, replacement of first-generation fluorite by barite, phlogopite and REE minerals, alteration of fluorite along crystal edges, cataclasis of barite and replacement by carbonates (including bastnaesite) and chalcedony.

Tab. 2: Representative analyses of REE ores from Kizilcaören.

Sample No.	P_2O_5	SrO	BaO	SO_3	ThO_2	CaO	F	La_2O_3	Ce_2O_3	Nd_2O_3	Sm_2O_3	Total
SK-2-E -6	0.287	0.887	0.149	0.274	0.803	2.043	10.836	21.895	25.865	5.524	0.621	71.186
SK-2-F -2	2.484	0.089	0.099	0.000	0.880	34.872	33.744	12.366	11.603	2.112	0.393	98.641
Sk-4-F -1	0.932	0.502	20.558	4.097	1.635	34.950	20.183	1.840	4.675	1.898	0.033	91.299
SK-8-E -1	0.228	0.797	0.000	0.000	0.847	20.960	16.114	9.280	11.476	2.210	0.306	100.930
SK-8-F -1	3.191	3.254	0.000	0.063	0.960	0.000	0.000	11.072	11.363	1.207	0.124	100.348
-4	2.950	3.584	0.036	0.091	0.714	33.371	30.307	14.156	12.248	1.343	0.474	99.275
-5	2.197	1.999	0.094	0.232	0.972	31.772	32.594	14.458	13.794	1.741	0.224	100.078

The final, third phase of mineralization deposited manganese and iron oxides and hydroxides, and may have remobilized carbonates and phosphates of the REE.

From the economic point of view, particular interest attaches to the quantitative distribution of rare earth elements in the ore. Bastnaesite (REE) FCO_3 and florencite ($CeAl_3[(OH)_6|(PO)_2]$) carry, in average, 20 wt.% REE (Tab. 2). In addition to these discrete minerals, REE also occur in the fine-grained second-generation fluorite matrix; individual fluorite grains show up to 0.34 wt.% La and 0.37 wt.% Ce. The matrix has been examined using broad-beam (50 μm) microprobe analysis; in view of the limitations of this analytical approach, the maximum values obtained are semiquantitative; they are (all in wt.%) La 14.5; Ce 12.6, Y 0.5 and in some samples, Nd 5.5 and Sm 0.65. Some representative analyses are given in Table 2. Values for Yb, Lu, Tb, Eu and Tm are below the detection levels of the microprobe.

Estimates of the distribution of major minerals in the Kizelcaören deposits gave fluorite 30 to 70%, barite 30 to 70%, matrix 0 to 30%, phlogopite 0 to 10%. Reserve estimates for the deposits of the Kizelcaören area have been given by GÜNALAY (1970), DEMIRÖZ (1976) and KAPLAN (1977). There are 380.000 t ThO_2 ore with an average grade of 0.2% and four million t of REE (Ce, La, Nd) and Y ores with an average grade of 3%. The fluorite and barite reserves have not been established quantitatively, but are estimated to be in the order of 10 million t.

Summary and Conclusion

The results presented in this note suggest a genetic link of fluorite-barite-REE mineralization with alkali volcanism (trachytes, phonolites, carbonatites) and with the development of the Aegean Rift in late Tertiary-Quaternary times. The high concentration of Ba and some REE in trachytes, phonolites and tuffs point to a parental magma primarily enriched in these elements. Hydrothermal systems generated by volcanic activity were responsible for transporting the elements and depositing them in suitable structures, resulting in the formation of vein and lens-type deposits.

The depositional environment of stratiform ore lenses in pyroclastic rocks has, of course, raised the question whether mineralization might have occurred under marine conditions. The presence of tuffs might point in that direction, and the sulphur isotope ratio of one barite sample has been investigated, giving a $\delta^{34}S$ of

+5.4‰. Limited though the value of a one-sample test may be, it cannot be used to support participation of seawater sulphate. Lens-type mineralization is therefore assumed to have taken place in shallow continental lakes.

This is a rare type of mineralization; the only occurrence which appears to be similar is Gallinas Mountains, New Mexico (PERHAC & HEINRICH, 1964). There, hypabyssal alkali intrusives of Tertiary age have led to fluorite-bastnaesite mineralization in epithermal veins and breccia fillings in Permian sandstone; formation temperatures are estimated to be in the order of 200° C. Fluorite is the dominant constituent contributing 53 to 86% of the bulk, followed by barite with 5.2%, bastnaesite with 0.2 to 5% and a few percent quartz and barite. Detailed isotopic and fluid inclusion work on Kizilcaören material will assist in quantifying the physicochemical parameters of ore deposition.

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