Trace and Rare Earth Element Geochemistry of Black Shales in Triassic Kasımlar Formation, Anamas-Akseki Platform, Western Taurids, Turkey

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Abstract. The Triassic black shale sequence of Kasımlar Formation in the Anamas-Akseki Platform, Western Taurids, Turkey do not show any trace element enrichment. But trace element values of Black shales from the Kasımlar Formation are broadly comparable with those of the average upper continental crust. While there are slightly enrichments in As, Bi, Zn, Nb, Cu, Pb, Cs and Sb. The other elements are slightly depleted in black shales according to those of upper continental crust (UC). Organic carbon content of the black shales is between 0.05 and 0.71 % but reach 3.78 % (averaging as 0.52 %). The black shales do not show metal/TOC correlation. Compared to the black shales of Kasımlar Formation and upper continental crust; The black shales show a significant increase in HREE and LREE. Our data show slightly negative Ce anomalies (Ce/Ce* as low as 0.94) and positive Eu anomalies (Eu/Eu* as high as 3.33). Ce/Ce* and Eu/Eu* values recorded in the depositional environment indicate low oxygenated and anaerobic (reducing) conditions.

1. Introduction
Black shales, which are rich in organic matter, are important for the natural fuel-resource economy of the world. Most shales contain 1 % or more organic carbon; 2-10 % is a common range. A few shales contain more than 20 % organic carbon [1]. Source rock potential of the oil-producing rocks of marine origin to the limit values in order to have sufficient organic carbon is 0.3 % wt. [2]. Black shales, as well as being rich in organic matter, are rich in metals and sulfides. Black shales are important as syngenetetic hosts for metal deposits. The Kupferschiefer of Peronian age in Central Europe is a good example of a metal enriched black shale, containing a few percent Cu and Pb. The lead-zinc deposits at Rammelsberg in West Germany are in organic-rich rocks of Devonian age. Oklo, uranium deposits in Africa, may represent a maximum concentration of uranium in which black shale. In Sweden, Alum shales of Cambrian age containing about 14 % organic carbon have been used as a source of pyrolysis oil and uranium [1, 3]. Black shale is an important host for redox sensitive metals such as Mo, Ni, V, U, Re and a number of other elements including Cu, Pb, Zn, Au, Hg, Sb etc. [4, 5, 6]. Triassic aged Kasımlar shale, which is the subject of this study, spreads in southeast of Isparta province. Kasımlar black shale may be thought an oil shale and rich in organic matter. The black shale has been investigated in terms of total organic carbon and major, trace and rare earth element geochemistry.

2. Geological setting
The area is situated on east part of Isparta Angle, in the Middle Taurus. Isparta angle is composed of autochthonous and allochthonous stratigraphic units. Autochthonous units form from Beydağları and...
Anamas - Akseki. Allochthonous units consist of Antalya, Beyşehir-Hoyran and Likya nappes [7]. In the study area, in the range of Cambrian - Tertiary aged, allochtonous and autochtonous, sedimentary, metamorphic and igneous rocks units are observed. Autochthonous units are composed of Paleozoic aged metamorphic, Mesozoic aged detritic and carbonate rocks and Tertiary detritic sediments. Allochtonous units consist of Antalya nappes which form pelagic and nericite sediments, ophiolitic rocks and platform type carbonates [8]. In the area, Black shales are observed in different two formations; a) Kasımlar Formation b) Isparta Çay formation. While Isparta Çay formation belongs to Antalya nappes, Kasımlar Formation occurs within Karacahisar autochtonous. Kasımlar Formation mainly consists of shale and sandstone units. The formation starts mostly conglomerate and sandstone in the lowest level and continues with the siltstone and dark gray - blackish shale. Unit, in the middle - upper levels has black and blackish shale and locally brecciated limestone lenses with abundant alg. The uppermost level of Kasımlar Formation consists of greenish claystone and with them intercalated platy limestones. The age of the Kasımlar Formation is Carnian - Norian. It is thicknes about 1300 - 1500 m [8].

3. Material and method
For the study 21 samples were collected from Kasımlar black shales. Each sample was prepared individually for organic and inorganic analyses. These analyses were conducted at Acme Analytical Laboratories Ltd. (Canada) using ICP-MS techniques. In order to determine the relation between the elements and organic material, Total Organic Carbon (TOC) analysis was performed for 21 samples. TOC (%) analysis was conducted at Geochemistry Laboratories of Turkish Petroleum Corporation (TPAO) by the pyrolysis method using the Rock-Eval 6 analyzer. IFP 160 000 (Institut Français du Petrole) was used as standard.

4. Total organic carbon (wt.% TOC) values in back shales of Kasımlar Formation
The TOC values of black shale samples are not rich in organic carbon. The values are mostly below 1 %. TOC values in shales ranges from 0.06% (KS11 sample) to 3.78 % (KS8B sample) (Avg. 0.52%) Average quantities of major oxides by weight of Kasımlar black shales are SiO₂ 57.60 %, Al₂O₃ 14.25 %, Fe₂O₃ 7.25 %, MgO 2.03 %, TiO₂ 0.79 %, P₂O₅ 0.16 %, CaO 5.31 %, Na₂O 1.14 % and K₂O 2.43 %). By evaluating major oxides values, it can be said that black shales have more kaolin and less illite and smectite group clays. The high ratio of K₂O, indicate presence of illite and Na₂O, MgO, Fe₂O₃ in Kasımlar black shales which also show to smectite group clays. So this, black shales contain different clay group minerals. Therefore, black shales have been formed by precipitation and transportation of detritic material that came out weathering of different originated rocks.

5. Trace element geochemistry
According to results of the analysis (Table 1), average trace element values of the black shales are correlated with average values of Upper Crusts' (UC) and average trace element values of Europian shales [9]. The comparison of the average trace element values of the black shales with the UC trace element values indicates that, As, Bi, Zn, Nb, Cu, Pb, Cs and Sb values in the Black shales are slightly higher than the UC values (Table 1). However, Ba, Be, Co, Rh, Sn, Sr, Ga, Hf, Th, U, V, W, Zr, Ni and Mo concentrations in Black Shale are lower than those of the UC. Ta and Cd concentrations are nearly similar to those of the UC (Table 1). The mobilization, precipitation and concentration of some multi-valance elements such as Mn, V, Cr, Mo, U, Th, Co and Ni are generally controlled by redox-sensitive metals [10, 11, 12, 13]. The above mentioned element values show a slight decrease with respect to those of UC (Table 1). The Sr/Ba ratio of the black shales of Kasımlar Formation is 0.53.

The solubility of SrSO₄ is relatively high, and thus Sr is assumed to migrate and precipitate in the center of the open marine basin or saline lake. Therefore, the ratios of Sr/Ba gradually increase from the coast to the center of the Lake/sea. In general, the Sr/Ba ratios greater than 1.0 commonly indicate saline water [14, 15, 16, 13]. The Sr/Ba ratio of the black shales of Kasımlar Formation is less than 1.0, indicating the influence of marine transgression is limited to insignificant.
| Element | Ba | Be | Co | Cr | Cs | Ga | Ge | Hf | Nb | Ni | Pb | Ru | Sb | Se | Sr | Ta | Th | Ti | Tl | Tm | U | V | W | Zr |
|--------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Value   |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |    |
| Kasımlar Black Shale | 301 | 3 | 148 | 5.8 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 | 18.2 |
| UC Values | 302 | 3 | 149 | 6.2 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 |
| Average | 303 | 3 | 149 | 6.2 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 | 19.7 | 20.9 |
| Samples   | La     | Ce     | Pr     | Nd     | Sm     | Eu     | Tb     | Yb     | Lu     |REE values (as ppm) in Kasınılar black shale and Ce/Ce*, Eu/Eu* values normalized with PAAS, UC, ES and Chondrite |
|-----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------------------------------------------------|
| KS-01     | 34.09  | 8.62   | 0.21   | 0.12   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-02     | 38.06  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-03     | 50.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-04     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-05     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-06     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-07     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-08     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-09     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-10     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-11     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-12     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-13     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-14     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-15     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-16     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-17     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-18     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-19     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |
| KS-20     | 40.00  | 8.50   | 0.21   | 0.13   | 0.01   | 0.02   | 0.00   | 0.01   | 0.00   | 0.01   |

**Table 2.** REE values (as ppm) in Kasınılar black shale and Ce/Ce*, Eu/Eu* values normalized with PAAS, UC, ES and Chondrite.
6. Rare Earth’s elements

Table 2 presents the analytical results of the rare earth elements (REE) of the Kasımlar black shales. Their average concentrations in the Upper Crust (UC) also are listed for comparison. The content of $\Sigma$REEs varies between 64.54 and 230.76 ppm, with the average of 158.07 ppm. Most of the samples have higher $\Sigma$REE contents than in UC. The concentration of the light REEs (LREEs = La + Ce + Pr + Nd + Sm + Eu) is higher than that of the heavy REEs (HREEs = Gd + Tb + Dy + Ho + Er + Tm + Yb + Lu). The arithmetic average of 21 samples of the REE, LREE, HREE values are 158.07, 139.79 and 18.28 ppm respectively. All these values show an increase with respect to those of the UC (Table 2). However, while the average ratio of LREE/HREE is 7.86 in black shales of Kasımlar formation, this ratio is 9.54 in the UC. This ratio indicates an increase in HREE content terms of those of the UC. Table 2 presents correlations between REE and TOC. Although there is no correlation exists between TOC and REE. This result indicates that organic materials are not responsible for the abundance of REEs.

6.1. Paleoredox conditions of depositional environment in Triassic Kasımlar Formation

Rare earth elements were evaluated according to minor elements content and according to REE contents in addition to demonstrate clearly composition Triassic Kasımlar Formation.

6.2. Results

6.2.1 According to minor element contents - the elements can be enriched as sulfides, hydroxides and oxides form depending on the redox conditions in depositional environments. To determine paleoredox conditions; Ni/Co, V/Cr, V/V+Ni and U/Th ratio was used [17]. It has been suggested that Ni/Co ratio represent <5 oxic conditions, 5-7 suboxic conditions and >7 to anoxic from suboxic depositional environments, [18]. V/Cr ratios <2 where the oxic conditions, from 2 to 4.25 between the dionic and >4.25 for the cases that the suboxic from anoxic changing conditions and >0.84 the oxic conditions represented [19]. However, V/V+Ni ratio <0.46 oxic environments that; 0.46 - 0.60 dionic; changing conditions from anoxic to oxic are represented that the values are between 0.54 and 0.82. And 0.84 represents euxinic conditions [19]. It is reported that U/Th ratios represent; <0.75 value oxic; dionic terms of values between 0.75 - 1.25,>1.25 represents changing depositional environments from suboxic to anoxic [20]. The U/Th ratios are widely used to decipher depositional redox conditions of sediments. The U/Th, Ni/Co, V/Cr values of the black shale of the Kasımlar Formation are 0.23, 3.07 and 2.69 respectively, indicating oxic depositional environment. In addition, V is generally enriched under anoxic conditions [13, 21], commonly with (V/V+Ni) >0.6, V/C> 2.0 [22, 18, 19]. As shown in Table 1, two ratios of the Kasımlar black shales are 0.71 and 2.69 respectively, indicates anoxic conditions.

6.2.2. According to REE contents, the depositional environment of the Black Shale of Kasımlar Formation is represented by oxic - anoxic conditions. The slightly negative Ce and positive Eu anomalies (Table 2) and Ce/Ce* and Eu/Eu* (Table 2) ratios indicate low oxic - anoxic (reducing) conditions.

7. Conclusions

This article contains a first systematic study on trace elements and REE compositions of Kasımlar black shales. In the study their geochemistry and their geological implications are discussed. The results of the study indicate:

- The trace elements are generally similar those of the UC, except Zn and As. Zn and As are higher than those of the UC.
- Average values of TOC in Upper Triassic Kasımlar black shales are 0.52 %.
- The average content of REE of Kasımlar black shales are generally higher than those of the UC, while normalized to UC [23]. The Post-Archean average Australian Shale (PAAS), European shale (ES) and samples of Kasımlar have been investigated to redox conditions in depositional environments. Kasımlar black shales have deposited in conditions oxic and anoxic.
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