



REE Tetrad Effect as a Powerful Indicator of Formation Conditions of Karst Bauxites: A Case Study of the Shahindezh Deposit, NW Iran

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Abstract: Study of the concentration of major, trace, and rare earth elements (REE) in the Shahindezh karst bauxite deposit, northwestern Iran clarifies the relationship of the tetrad effect with geochemical parameters in the bauxite ores. The existence of irregular curves in the chondrite-normalized REE patterns as well as non-CHARAC behavior of geochemically isovalent pairs (Y/Ho) are related to the tetrad effect. The meaningful positive correlation between the sizes of the calculated T_3 tetrad effect and some geochemical factors such as Y/Ho, ΣREE , La/Y, (La/Yb)_N, and (LREE/HREE)_N as well as some major oxides-based parameters like $\text{Al}_2\text{O}_3 + \text{LOI}/\text{SiO}_2 + \text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3 + \text{LOI}$, IOL, and $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ indicate that the studied bauxite horizon was likely deposited by different (acidic and/or alkalic) solutions at different stages. The lower part of the studied horizon with a thickness of ~4.7 m displays alkali characteristics whereas the upper parts of the horizon with a thickness of ~5.3 m are characterized by more acidic conditions. These results are fully supported by the co-occurrence of convex-concave tetrad effect curves in the chondrite-normalized REE patterns. Therefore, the tetrad effect phenomenon used in this study has proved to be a good and reliable geochemical proxy to assess the conditions of the depositional environment in the Shahindezh bauxite ores.

Key words: Geochemistry, REE, Tetrad effect, Karst bauxite, Shahindezh, Iran

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1 Introduction

Recent studies have shown that rare earth elements (REE) display similar behaviors during geochemical processes in natural systems. Their different reactions to various geological environments make them useful as a powerful indicator for interpreting paleochemical conditions in an extensive geological environment. The ionic radii of REE vary from La (1.03 Å) to Lu (0.86 Å); REE are also found commonly in 3⁺ oxidation states (except Ce and Eu) in various geological environments (Shannon, 1976; Constantopoulos, 1988; Lottermoser, 1992; Kawabe, 1995). The lanthanide contraction (decreasing ionic radius with increasing atomic number), different oxidation states in two of them (Ce³⁺/Ce⁴⁺ and Eu²⁺/Eu³⁺), the tetrad effect due to increase in stability at quarter, half, three-quarter, and full filling of 4f orbital of lanthanides (Jahn et al., 2001), are the most well-known specifications that control REE distribution in various geochemical processes and geological environments (McLennan, 1994; Monecke et al., 2000 and references therein).

REE mobilization depends on concentration of anions/ligands (e.g., hydroxyl, chloride, fluoride, carbonate, and sulfate) and the stability of REE with these ligands in aqueous systems (Migdisov et al., 2016). Despite having

coherent behavior, REE are strongly sensitive to physical and chemical conditions of the environment such as pH, Eh, adsorption, desorption, and availability of mineral phases such as Fe- and/or Mn-oxides (hydroxides) in solutions (Davranche et al., 2005). In general, ionic charge and radius of REE control their geochemical behaviors and hence distribution patterns in geological environments; this is the so-called CHARAC (CHARGE and RADIUS CONTROL) behavior (Bau, 1996). Despite having similar geochemical behaviors, REE fractionation in aqueous systems is quite common, and has been reported from different geochemical environments by many researchers (Nardi et al., 2012; Lee et al., 2013; Abedini et al., 2017; Rezaei Azizi et al., 2017; Abedini et al., 2018a,b).

During evolution of geochemical systems, a smooth normalized REE distribution curve is thought to be observed because of about 17% linear decrease in ionic radii of REE, known as the lanthanide contraction (Peterson and Cunningham, 1967). Nevertheless, irregular patterns in the normalized REE distribution patterns from various geochemical systems as an indicator during geochemical processes have been observed and named the tetrad effect for the first time by Peppard et al. (1969). This feature known also as the ‘double-double effect’, ‘kinked effect’, or ‘zigzag effect’ in the literature is used

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as a new geochemical/mathematical-based tool to interpret irregular curves in normalized REE distribution patterns in a wide range of deposits (Kawabe, 1995; Lee et al., 1994; Irber, 1999; Jahn et al., 2001; Broska et al., 2006; Feng et al., 2011; Cunha et al., 2012; Nardi et al., 2012; Cao et al., 2013; Lee et al., 2013; Duc-Tin and Keppler, 2015; Abedini et al., 2017; Rezaei Azizi et al., 2017; Abedini et al., 2018a). Lee et al. (1994) went on to suggest that the zigzag pattern of normalized REE patterns are indicative of an imperfect tetrad effect phenomenon in geochemical systems.

The existence of the tetrad effect in normalized REE distribution patterns can be distinguished by the presence of convex and/or concave forms of curves in four discrete groups of REE. These groups are named as first, second, third, and fourth tetrads representing four groups of rare earth elements, (1) La-Ce-Pr-Nd, (2) Pm-Sm-Eu-Gd, (3) Gd-Tb-Dy-Ho, and (4) Er-Tm-Yb-Lu, respectively (Kawabe et al., 1991; Kawabe, 1992; Irber, 1999; Feng et al., 2011). The boundary points between tetrads represent the degree of filling in the $4f$ orbital corresponding to quarter (first tetrad), half (second tetrad), three-quarter (third tetrad), and completely filled (fourth tetrad), respectively (Jahn et al., 2001). Among REE, Gd is the only common rare earth element that belongs to both second and third tetrads (Kawabe, 1992). The refined spin-pairing energy theory (RSPET) (Jørgensen, 1970), the ligand-field theory caused by electrostatic forces influencing variation of bonding energy known as the nephelauxetic effect (Censi et al., 2007), the quantum-based Gibbs free energy (GFE) theory (Kawabe et al., 1999), and the electron configuration of REE (Masuda et al., 1994) are mostly used as the main physico-chemical-based theories for the occurring tetrad effect phenomenon in geochemical processes.

During alteration and weathering of Al-bearing rich minerals such as feldspars of parent rocks, authigenic bauxites are deposited in tropical to subtropical climates (rainfalls of ~1200 cm/year and temperatures of ~22°C) (Bogatyrev and Zhukov, 2009; Mondillo et al., 2011; Yuste et al., 2015). Lateritic bauxite, Tikhvin-type bauxite, and karst bauxite deposits are the main classifications for bauxite deposits (Bardossy and Combes, 1999). Previous studies have shown that the bauxite deposits of the world are scattered around the northern Mediterranean coast, Caribbean basin, East-Asia, Irano-Himalaya, North America, southwest Pacific, and finally Urals-Siberia-Central Asia belts (Bardossy, 1982; Bardossy and Aleeva, 1990). In recent years, many studies worldwide have been conducted by researchers to investigate the REE geochemistry of bauxite deposits (Ling et al., 2013; Mongelli et al., 2014; Peh and Kovacevic Galovic, 2014; Liu et al., 2016; Mongelli et al., 2016; Gamaletsos et al., 2017; Hou et al., 2017; Long et al., 2017; Mongelli et al., 2017; Torró et al., 2017; Chen et al., 2018; Ling et al., 2018).

Most bauxite deposits in the Irano-Himalaya karst bauxite belt were deposited from Permian to Cretaceous (Abedini and Calagari, 2014). The Shahindezh bauxitic horizon is located about 10 km east of Shahindezh city, West-Azarbaidjan province, NW Iran. The bauxite

deposits in NW Iran have been studied in detail by many researchers (Calagari and Abedini, 2007; Calagari et al., 2010; Abedini and Calagari, 2013a, b, c; Abedini et al., 2014; Khosravi et al., 2017). So far, except for the Kanigorgeh Ti-rich bauxite in Iran (Abedini et al., 2018a), the presence and occurrence of the tetrad effect in the normalized REE distribution patterns of bauxite deposits around the world have not been investigated in detail.

In this research, we focus on the behavior of REE and some isoivalent geochemically similar trace elements such as Y-Ho, Zr-Hf, and Nb-Ta to find out the probable relationship between the tetrad effect phenomenon and these geochemical pairs in the Shahindezh bauxite horizon. We also use this phenomenon as a new and useful geochemical tool to assess and interpret the formation conditions of bauxite deposits.

2 Previous Work and Geological Setting

Many of the bauxite deposits in NW Iran are located in the Irano-Himalaya karst bauxite belt (Abedini and Calagari, 2014). The Permian carbonates hosting the Shahindezh bauxite horizon are unconformably overlain by a Mesozoic sequence. Many epeirogenic movements that took place in the late Permian brought about various hiatuses in the Permian carbonates of the studied district, and were followed by some basic volcanic activity in NW Iran (Abedini and Calagari, 2013c and references therein). Several uplifts during the late Permian and the ensuing marine regression over a NW–SE trending belt in Iran were followed by the development of some lateritic and bauxitic horizons.

The Shahindezh bauxite horizon is located in about 10 km east of Shahindezh city, West-Azarbaidjan province, NW Iran. The geologic features and lithologic details of this district and the surrounding districts are discussed in previous works (Abedini and Calagari, 2013c; Abedini and Calagari, 2015). Based upon the tectonic and structural divisions of Iran (Alavi 1991; Aghanabati 1998, 2005), the Shahindezh bauxite horizon is a part of the Sanandaj-Sirjan magmatic metamorphic zone (Fig. 1). Lithologically, the surrounding rocks in this district are as follows: (1) the Precambrian sequence (shale, dolomite, and limestone); (2) the Cambro-Ordovician Mila Formation (sandstone, dolomite, limestone, and shale); (3) the lower Permian Dorud Formation (sandstone, shale, and diabase); (4) the middle-upper Permian Ruteh Formation (dolomite, limestone, diabase, and lenses and layers bauxite ores); (5) the Triassic Elik Formation (carbonate and andesite); (6) the Triassic–Jurassic bauxite ores; (7) the Jurassic Shemshak Formation (sandstone, shale, claystone, marl, and siltstone); (8) the Cretaceous units (sandstone, limestone, and shale); (9) the Miocene Qom Formation (limestone, conglomerate, limestone, and various kinds of volcanics); and (10) the Plio-Quaternary units (conglomerate with sandy and gritty horizons) (Fig. 2a).

There are two main groups of bauxite ores occurring as discontinuous NW–SE, NE–SW, and N–S trending layers and/or lenses: (1) a Permian bauxite in upper Permian carbonate bedrocks; and (2) a Triassic–Jurassic age

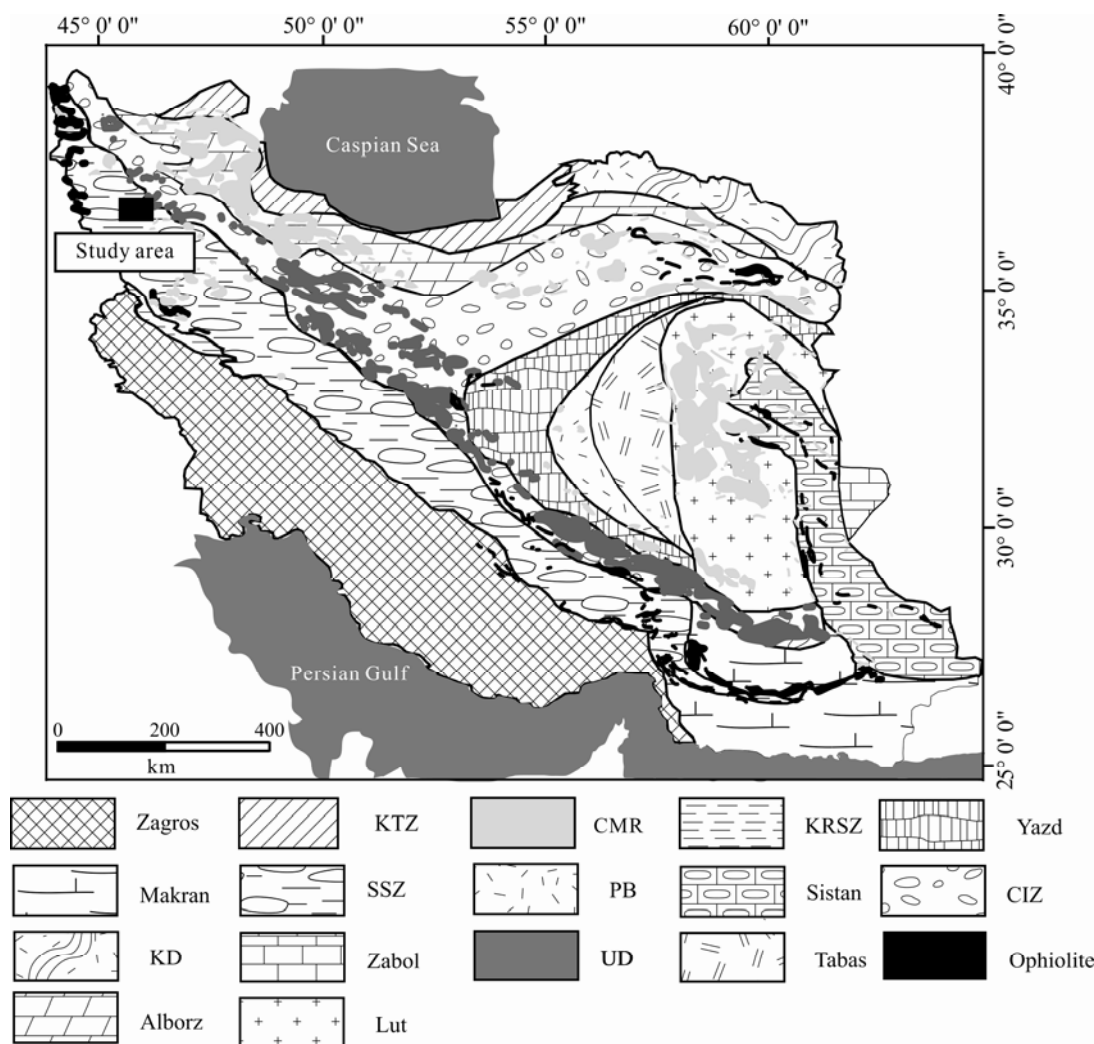


Fig. 1. A simplified tectonic and structural map of Iran (modified from Alavi 1991; Aghanabati 1998, 2005) showing the Shahindezh bauxite horizon district.

Zagros: Zagros mountain ranges; KRSZ: Kermanshah; Radiolarites subzone; SSZ: Sanandaj-Sirjan magmatic metamorphic zone; UD: Urumieh-Dokhtar magmatic arc; CIM: Central Iranian microcontinent (includes Yazd, Posht-e-Badam block (PB), Tabas, and Lut blocks); Alborz: Alborz ranges, western Alborz-Azarbaijan; KTZ: Khazar-Talesh-Ziveh structural zone; CIZ: Central Iranian zone; Sistan: East Iran ranges; Makran: Makran zone; KD: Kopeh-Dagh ranges; Zabol: Zabol area; and CMR: Cenozoic magmatic rocks.

bauxite along the border of the Triassic dolomite and the Jurassic sandstone in this district. Based on field observations and certain physical specifications, three subdivisions are recognized in the selected profile. First, a bauxite layer in the lower part of the horizon, which is characterized by its red to brownish-red color (RBRB) with a thickness of about 4.8 m. The second part lies in the middle of the horizon and is characterized by a green to greenish-cream (GCB) color and has a thickness of about 3 m. The third part of the horizon lies at the top and has a thickness of about 2.2 m and varies in color from white to pink (WPB) (Fig. 2b).

Mineralogically, the bauxite ores of the studied horizon consist of diasporite, boehmite, kaolinite, hematite, goethite, rutile, illite, montmorillonite, chlorite, and quartz. Abedini and Calagari (2013c) postulated that an authigenetic origin and allotritic type for the studied bauxite deposit. Meanwhile, this deposit comprises a bauxitic iron body, a bauxitic clayey iron body, clayey

bauxite, and finally bauxitic clay mineralogical features. The diabasic rocks cropping out in the studied district were recognized to be the potential precursor for the ores, which were deposited authigenically (Abedini and Calagari, 2013c). This unit includes feldspar (plagioclase and a lesser amount of K-feldspars), ferromagnesian (augite and olivine with partial alteration to chlorite), opaque minerals (pyrite and ilmenite), and some accessory mineral phases such as apatite and zircon.

3 Methodology

In order to investigate the bauxite ores, a sampling profile (A-B in Fig. 2) was selected across the Shahindezh bauxite horizon, and 21 representative samples were systematically collected at ~0.5 m intervals on the basis of color changes. Of these, ten samples (B-1 to B-10) are from the red to brownish-red ores, six (B-11 to B-16) from the green to greenish-cream ores, and five (B-17 to B-21)

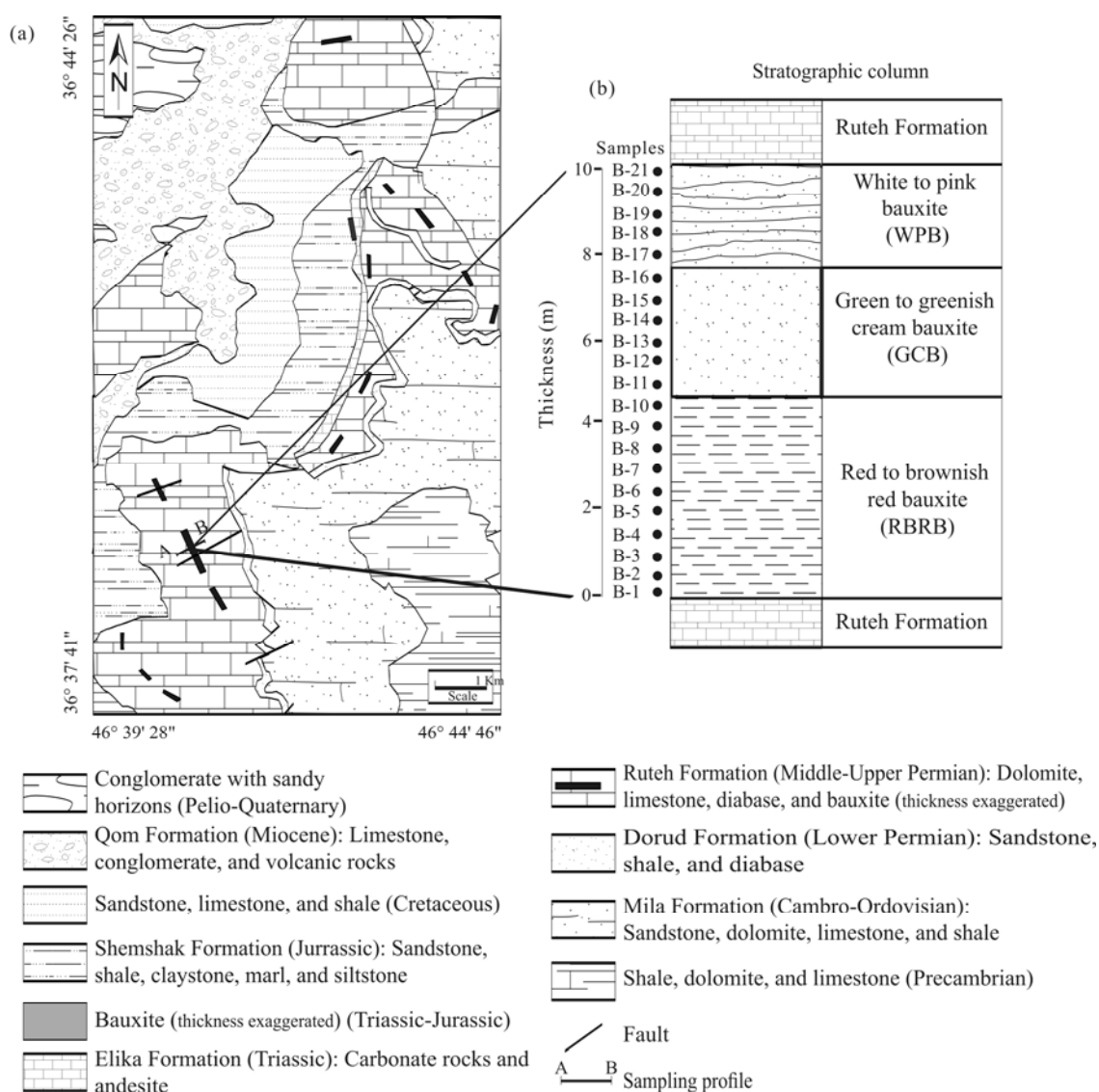


Fig. 2. (a) Geological map of the study area covering the locations of various bauxite horizons and their host rocks; (b) stratigraphic column of the Shahindezh bauxite horizon showing position of the collected samples.

from the white to pink ores.

For chemical analysis, all of the collected samples were dried at 60°C, and then were crushed to less than 200 mesh in the laboratories of ALS Cemex, Canada, using an agate mill: 0.2 gram of each sample was weighed in a graphite crucible; 1.5 gram of $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ flux was added to each weighed sample. These mixtures were heated in a furnace for thirty minutes at 980°C. After cooling, all samples were dissolved in 100 ml of nitric acid (5%). The samples were poured into a polypropylene tube for measurement. In order to test, calibration standards, reagent blanks, and verification standards were included in the measurement processes. The major oxides were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). In this method, the detection limit values for SiO_2 , Al_2O_3 , Fe_2O_3 , and LOI are 0.04, 0.03, 0.04, and 0.1 wt%, respectively, and the limit for CaO , MgO , Na_2O , K_2O , TiO_2 , MnO , and P_2O_5 is 0.01

wt%. The values of LOI (loss on ignition) for all samples were calculated by measuring weight loss of 1 gr sample before and after heating at 950°C for ninety minutes. The values of REE were determined by using inductively coupled plasma-mass spectrometry (ICP-MS) as well. The values of detection limits for Pr, Nd, Sm, Tb, and Lu are 0.02, 0.4, 0.1, 0.01, and 0.01 ppm, respectively. The detection limit for other REE is 0.05 ppm. In this research, all REE values were normalized relative to chondrite values from Anders and Grevesse (1989). All the computations and plots in this research were carried out by using MATLAB R2016b software (MATLAB User's Guide, 2016).

4 Results

4.1 Major element concentrations

The concentration values of major elements in the

studied samples are listed in Table 1. According to this table, the concentration values for SiO₂ and Al₂O₃ in the bauxitic samples vary within the range of 1.3–44.2wt% and 17.4–51.2wt%, respectively. The concentration values of Fe₂O₃ ranges from 2.2wt% to 69.4wt%. The values of CaO and MgO display very narrow variations, which are within the range of 0.12–0.22wt% and 0.02–0.22wt%, respectively. Similarly, the Na₂O, and K₂O values also exhibit narrow variations within the range of 0.04–0.79 wt% and 0.05–0.91wt%, respectively. The TiO₂, MnO, and P₂O₅ contents are within the range of 2.14–3.74wt%, 0.01–0.04wt%, and 0.02–0.21wt%, respectively.

4.2 Intensity of lateritization (IOL)

The degree of lateritization in bauxite deposits are customarily characterized by IOL (intensity of lateritization) using the following equation (Babechuk et al., 2014):

$$IOL = [(Al_2O_3 + Fe_2O_{3(T)}) / (SiO_2 + Al_2O_3 + Fe_2O_{3(T)})] \times 100 \quad (1)$$

The size of calculated IOL in all of the bauxite samples in the studied district shows a noticeable variation ranging from 48.18% to 98.52 % with an average of 66.65% (Table 1).

4.3 REE concentrations in the bauxite ore samples

The concentration values of REE are listed in Table 2. The Y concentration values vary from 41.13 ppm to 65.49 ppm with an average value of 52.88 ppm (Table 2). The minimum and maximum values for Y/Ho ratio are 21.05 and 48.17, respectively (Table 2). According to Table 2, the ΣREE vary from 134.92 ppm to 398.22 ppm. The La/Y and (La/Yb)_N values vary within the range of 0.61–1.53 and 5.65–13.35, respectively (Table 2).

The Ce and Eu anomalies were computed using the following equations (Taylor and McLennan, 1985):

$$Eu/Eu^* = Eu_N / (Sm_N \times Gd_N)^{0.5} \quad (2)$$

$$Ce/Ce^* = 2 \times Ce_N / (La_N + Pr_N) \quad (3)$$

The chondrite normalizing values (N) are from Anders and Grevesse (1989). The calculated values of Ce/Ce* and Eu/Eu* vary from 0.67 to 1.37 and from 0.71 to 1.07, respectively (Table 2).

5 Discussion

5.1 REE distribution pattern in the bauxite ore samples

The concentration variations of REE and the chondrite-

normalized REE distribution patterns are illustrated in Fig. 3a, b. As shown in this figure, a remarkable increase in ΣREE is observed from parts GCB (B-11) to RBRB (B-10). Furthermore, the tetrad effect phenomenon with various shapes (both convex and concave) is observed in the chondrite-normalized REE distribution pattern. Besides, the diagram of frequency distribution of ΣREE (Fig. 4a) and Eu anomalies (Fig. 4b) display a bimodal diagram. As shown in Fig. 4a, a conspicuous gap (B-11) exists between ΣREE values in the lower part (RBRB) of the horizon and those in the upper parts (WPB and GCB). This means that the B-11 bauxite sample is probably located near the boundary of changes in depositional and/or alteration conditions. REE can be easily leached from weathered environments under low pH conditions and can be precipitated in alkaline environments (Nesbitt, 1979) by the presence of scavenging agents (e.g., Fe-oxides/hydroxides) that cause their fixation (Ohta et al., 2009; Sasmaz et al., 2014, 2017). Based on the analytical results, the relatively low SLREE values (average of 157.56 ppm) of the samples in the upper parts of the horizon (WPB and GCB) might be due to the leaching of these elements by low-pH meteoric origin percolating solutions from the weathering zone and their concentration (average of 321.13 ppm) in the lower part (RBRB) of the horizon, owing to a pH increase brought about by solution-carbonate bedrock interactions. Meanwhile, the average values of SHREE for samples from the upper parts (WPB and GCB) and the lower part (RBRB) of the horizon are 16.36 ppm and 21.3 ppm, respectively.

In the diagram of ΣREE versus Fe₂O_{3(T)} (Fig. 5), the ΣREE values display two different trends, which are consistent with acidic-alkali conditions during the formation of the upper and lower parts of the studied horizon. As shown in Fig. 5, the upper parts of the horizon (B-11 to B-21) have no meaningful correlation with Fe₂O₃ content but the trend changes in the lower part of the horizon (B-1 to B-10) in which the ΣREE values depict a conspicuous positive correlation with Fe₂O₃. This signifies that Fe-oxides are likely the main scavengers for fixing REE in the lower part of the horizon.

5.2 Interpretation of Ce and Eu anomalies in the studied bauxite samples

Variation of the Ce and Eu anomalies are illustrated in Fig. 6. The Ce and Eu anomalies generally depend on Eh (*f*O₂) and pH of solutions during deposition processes (Abedini et al., 2016). On the other hand, bauxite deposits

Table 1 Results of chemical analyses carried out by ICP-AES method for major (wt%) elements of bauxite samples from three different colored zones in the studied profile

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10	B-11	B-12	B-13	B-14	B-15	B-16	B-17	B-18	B-19	B-20	B-21
SiO ₂	1.3	24.2	21.2	28.4	15.1	18.5	8.9	30.2	28.1	13.7	24.9	34.1	32.3	38.4	27.9	30.7	43.2	42.3	44.2	41.6	42.9
Al ₂ O ₃	17.4	19.7	19.25	19.3	19.51	18.44	21.14	22.2	21.7	19.21	50.6	45.8	48.6	44.2	51.2	49.6	37.9	37.5	37.9	37.5	37.7
Fe ₂ O ₃	69.4	43.2	46.4	39.7	53.2	49.95	57.8	35.2	35.7	53.45	3.7	3.5	3.6	4.3	2.5	2.9	3.4	2.2	3.2	2.9	3.1
CaO	0.12	0.17	0.14	0.15	0.13	0.13	0.14	0.12	0.18	0.14	0.15	0.17	0.19	0.2	0.18	0.2	0.21	0.19	0.22	0.21	0.22
MgO	0.02	0.18	0.13	0.14	0.12	0.16	0.11	0.14	0.18	0.14	0.17	0.18	0.2	0.22	0.19	0.19	0.2	0.19	0.19	0.19	0.18
Na ₂ O	0.04	0.12	0.11	0.14	0.07	0.12	0.07	0.16	0.79	0.09	0.22	0.19	0.16	0.19	0.11	0.16	0.2	0.1	0.13	0.14	0.13
K ₂ O	0.05	0.49	0.41	0.53	0.25	0.36	0.15	0.6	0.91	0.25	0.19	0.24	0.29	0.37	0.26	0.27	0.29	0.26	0.3	0.25	0.26
TiO ₂	2.51	2.59	2.75	2.35	2.45	2.55	2.55	2.14	2.94	2.55	3.41	3.45	3.51	3.61	3.32	3.51	3.74	2.76	2.63	3.14	2.95
MnO	0.03	0.02	0.01	0.02	0.03	0.02	0.04	0.02	0.01	0.03	0.02	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01
P ₂ O ₅	0.18	0.17	0.14	0.13	0.19	0.15	0.21	0.08	0.09	0.16	0.04	0.04	0.03	0.04	0.04	0.04	0.05	0.02	0.04	0.03	0.03
LOI	8.61	8.97	9.32	9.06	8.92	9.47	8.82	9.06	8.95	10.21	16.58	13.25	10.85	8.42	14.21	12.25	10.7	14.4	11.12	13.9	12.5
Sum	99.66	99.81	99.86	99.92	99.97	99.85	99.93	99.92	99.55	99.93	99.98	100.93	99.75	99.96	99.92	99.83	99.91	99.93	99.94	99.87	99.98

were likely deposited under tropical to subtropical climates with temperatures around 22°C (Bogatyrev and Zhukov, 2009; Mondillo et al., 2011). Möller et al. (1998) suggested that the Eu anomaly strongly depends on temperature and pH of solutions. Under low fugacity of oxygen, Eu^{2+} is more dominant in the solutions and can easily produce a more stable Eu^{2+} -complex with aqueous anions such as CO_3 , CH_4 , HS^- , which causes positive Eu anomaly in precipitates. In contrast, oxidation of Eu^{2+} converts to Eu^{3+} under higher fugacity of oxygen and is characterized by negative Eu anomalies (Tang et al., 2013). Therefore, the higher fugacity of oxygen in the low pH meteoric solution causes increase the amounts of Eu^{3+} in the solutions reacted with parental rocks. Under these conditions, the mineral phases precipitated from such solutions can produce negative Eu in mineral phases. By taking the above premises, the Ce and Eu anomalies of the studied profile were likely influenced by oxygen fugacity

($f\text{O}_2$) and pH of the responsible solutions during bauxitization process.

The average values of Ce anomalies in different parts of the horizon are 1.22 for the RBRB, 0.85 for the GCB, and 0.97 for the WPB. Similarly, the average values of Eu anomalies in different parts of the horizon are 0.97 for the RBRB, 0.9 for the GCB, and 0.76 for the WPB. Therefore, it is obvious that both the Ce and Eu (Fig. 3b) anomaly values increase downward from the top toward the bottom of the horizon. Oxidation of Ce^{3+} to Ce^{4+} during weathering conditions strongly depends on pH and Eh of solutions in the depositional environment (Braun et al., 1990; Hill et al., 2000). Furthermore, Abedini et al. (2016) suggested that a negative Eu anomaly can be attributed to low pH of fluids/solutions during geochemical processes. This means that acidic meteoric solutions as a leaching agent affected the upper part of the bauxite horizon in the studied district. Based on the above-mentioned discussion,

Table 2 Results of chemical analyses (ICP-MS) for trace and rare earth elements (ppm) along with elemental ratios and tetrad values of bauxite samples from three different colored zones in the studied profile. ΣREE = total REE

	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	B-10	B-11	B-12	B-13	B-14	B-15	B-16	B-17	B-18	B-19	B-20	B-21
La (ppm)	68.4	62.4	64.8	68.4	64.8	67.2	65.7	70	68	64.2	38.5	40.1	38.7	45.1	32.6	35.2	34	29.6	31.4	40.1	35.2
Ce	174.2	155.6	154	142.1	162.4	152.4	165.2	137.5	151	160.2	110	74.2	48.7	58.6	43.8	75.3	67.2	59.7	59.6	50.1	54.1
Pr	12.64	13.35	13.05	13.85	12.45	12.76	11.5	14.8	11.02	12.2	10.09	7.45	6.54	9.26	4.97	8.7	9.6	4.96	5.94	5.91	5.96
Nd	65.2	50.1	49.3	52.1	46.8	48.8	51.6	54.9	64.2	47.4	50.1	46.2	42.5	38.7	28.3	39.1	43.6	21.3	23.4	32.6	27.5
Sm	18.1	10.4	11.54	10.45	13.74	12.74	14.91	10.55	13.2	11.82	9.66	7.41	6.53	8.75	4.23	6.5	8.71	5.22	5.69	5.12	5.32
Eu	7.88	3.24	3.94	3.12	5.45	4.64	5.65	3.02	4.02	5.145	2.51	2.11	1.75	2.29	1.22	1.97	2.13	1.29	1.39	1.31	1.33
Gd	27.8	11.6	13.89	10.4	18.7	16.18	22.25	9.78	11.4	19.2	7.5	6.51	5.6	6.94	4.66	6.02	7.11	5.03	5.12	6.11	5.62
Tb	1.45	1.57	1.44	1.48	1.49	1.42	1.47	1.42	3.21	1.42	1.32	1.01	0.85	0.71	0.71	0.99	1.2	0.66	0.81	0.79	0.76
Dy	9.21	9.11	8.6	8.1	7.45	7.22	8.45	7.4	6.92	6.88	7.14	4.1	7.04	6.65	5.84	5.74	7.9	4.84	5.36	4.98	5.21
Ho	2.41	1.54	1.65	1.47	1.87	1.71	2.13	1.43	2.11	1.98	1.61	1.25	0.91	0.93	0.88	0.96	1.52	1.01	1.07	0.99	1.03
Er	3.97	4.22	4.24	4.45	4.12	4.45	4.02	4.9	3.78	4.18	4.54	4.33	4.23	4.81	3.69	4.75	6.01	2.9	3.11	2.87	2.96
Tm	0.68	0.51	0.45	0.54	0.62	0.59	0.63	0.61	0.41	0.61	0.45	0.5	0.45	0.53	0.39	0.51	0.52	0.38	0.48	0.44	0.51
Yb	5.64	4.01	4.21	3.84	4.74	4.41	5.07	3.63	5.2	4.71	4.11	4.91	3.9	3.71	3.24	3.11	3.01	2.83	2.99	3.56	3.25
Lu	0.64	0.58	0.56	0.55	0.49	0.54	0.59	0.54	0.49	0.54	0.52	0.51	0.45	0.53	0.39	0.55	0.44	0.45	0.49	0.44	0.47
Y (ppm)	61.17	65.49	61.69	60.65	62.9	58.06	59.1	55.64	44.41	58.58	58.41	49.25	41.64	43.2	41.13	45.79	55.49	43.2	48.56	47.69	48.38
ΣREE	398.22	328.23	331.67	320.85	345.12	335.06	359.17	320.48	344.96	340.485	248.05	200.59	168.15	187.51	134.92	189.4	192.95	140.17	146.85	155.32	149.22
Ce anomaly	1.32	1.23	1.20	1.03	1.28	1.36	1.32	0.97	1.20	1.28	0.89	0.96	0.67	0.88	0.70	1.00	0.87	1.08	1.37	0.69	0.82
Eu anomaly	1.07	0.90	0.95	0.91	1.03	0.98	0.94	0.90	1.00	1.04	0.14	0.92	0.88	0.89	0.83	0.96	0.82	0.76	0.78	0.71	0.74
La/Y	1.12	0.95	1.05	1.13	1.03	1.16	1.11	1.26	1.53	1.10	0.66	0.81	0.93	1.04	0.79	0.77	0.61	0.69	0.65	0.84	0.73
Y/Ho	25.38	42.53	37.39	41.26	33.64	33.95	27.75	38.91	21.05	29.59	36.28	39.40	45.76	46.45	46.74	47.70	36.51	42.77	45.38	48.17	46.97
IOL	98.52	72.22	75.59	67.51	82.80	78.71	89.87	65.53	67.13	84.14	68.56	59.11	61.78	55.81	65.81	63.10	48.88	48.41	48.18	49.27	48.75
$\text{Al}_2\text{O}_3 + \text{LOI}$	26.01	28.67	28.57	28.36	28.43	27.91	29.96	31.26	30.65	29.42	67.18	59.05	59.45	52.62	65.41	61.85	48.60	51.90	49.02	51.40	50.20
$\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$	0.25	0.46	0.41	0.49	0.37	0.37	0.37	0.63	0.61	0.36	13.68	13.09	13.50	10.28	20.48	17.10	11.15	17.05	11.84	12.93	12.16
$\text{SiO}_2 + \text{Fe}_2\text{O}_3$	70.70	67.40	67.60	68.10	68.30	68.45	66.70	65.40	63.80	67.15	28.60	37.60	35.90	42.70	30.40	33.60	46.60	44.50	47.40	44.50	46.00
$(\text{Al}_2\text{O}_3 + \text{LOI})/(\text{SiO}_2 + \text{Fe}_2\text{O}_3)$	0.37	0.43	0.42	0.42	0.42	0.41	0.45	0.48	0.48	0.44	2.35	1.57	1.66	1.23	2.15	1.84	1.04	1.17	1.03	1.16	1.09

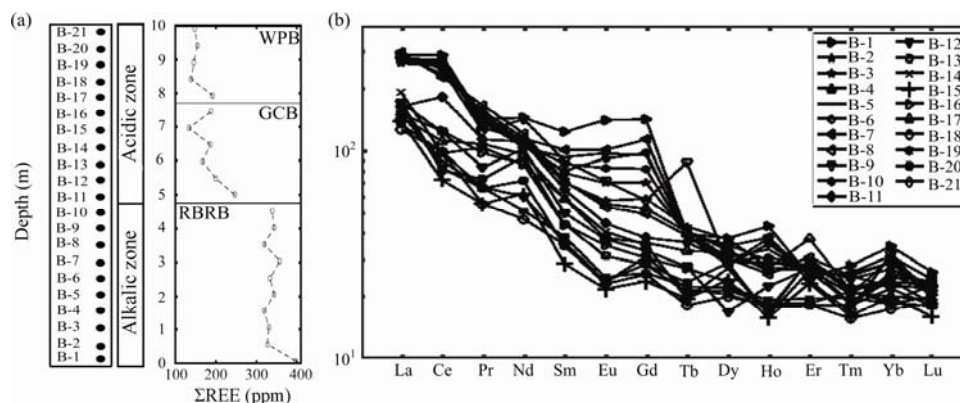


Fig. 3. (a) Distribution pattern of ΣREE across the studied profile; (b) chondrite-normalized REE distribution pattern for analyzed bauxite samples in the Shahindezh bauxite horizon. Normalization values for chondrite are from Anders and Grevesse (1989).

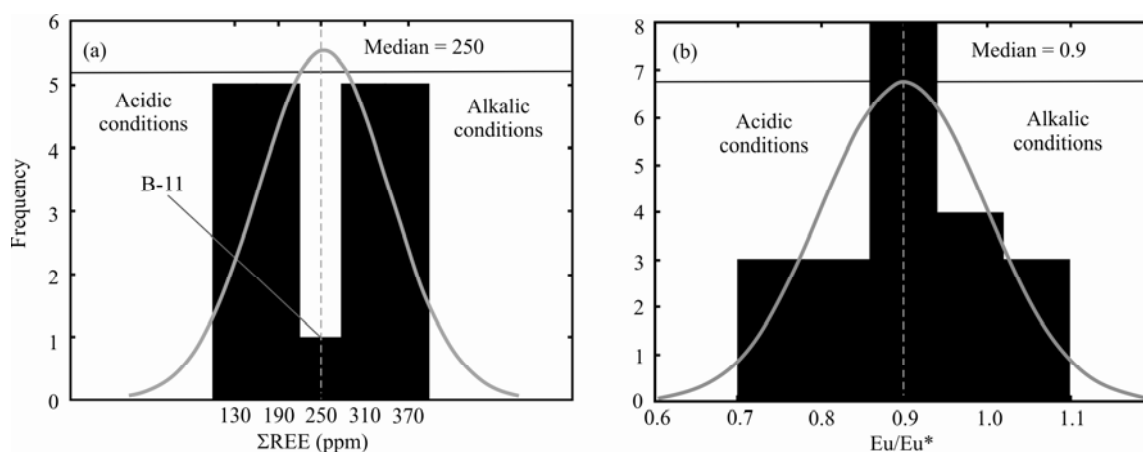


Fig. 4. Diagrams of frequency versus (a) ΣREE and (b) Eu/Eu^* values of bauxite samples in the studied profile.

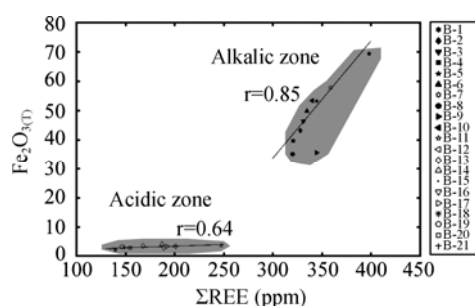


Fig. 5. Bivariate plot of ΣREE versus $\text{Fe}_2\text{O}_{3(\text{T})}$ in the bauxite samples of the studied district.

it can be concluded that the bauxite horizon in the studied district comprises two different parts which are characterized by an alkaline zone (in the lower part) with relatively higher positive Ce and Eu anomalies, and an acidic zone (in the upper part) with neutral to negative Ce and Eu anomalies. This implies that the pH of the solutions as well as the fugacity of oxygen in the studied district has probably played a crucial role during the distribution of REE and the occurrence of positive Ce and Eu anomalies.

5.3 Point of Zero charge (PZC)

Upon metal and aquatic interactions, surface sorption on metal-oxides (hydroxides) is considered as a geochemical process in many geological environments with a wide range of temperature (Hochella and White, 1990). Previous researches have proved that the point of zero charge (PZC) as a geochemical factor is a pH_{PZC} where positive and negative charges on the surface of metal oxides (hydroxides) are in equilibrium state with the lack of significant sorption (Schoonen, 1994). Therefore, positive charge on surfaces occurs at pH values under pH_{PZC} and the pH values higher than pH_{PZC} cause the surfaces to be negatively charged. This means that pH_{PZC} is an important geochemical parameter, which causes sorption of anions or cations on the surface of metal oxides such as Fe-hydroxides, hematite, goethite, ferrihydrite, and magnetite (Sverjensky, 1994; Kosmulski, 2011) from solutions and/or fluids.

Based on Coulomb's inverse-square law, when two

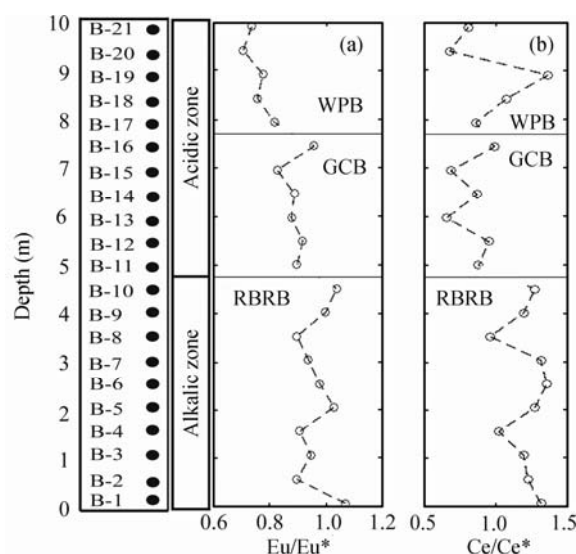


Fig. 6. Distribution patterns of (a) Eu/Eu^* and (b) Ce/Ce^* values in the bauxite samples across the Shahindezh bauxite horizon.

electric charges are the same, the electrostatic force between them is repulsive. However, electrostatic force between opposite charges is attractive. Although, the sorption between same charged ions has been reported based on specific bonds between them, repulsive electrostatic forces can be overcome (Parks, 1990). Many positive charge ions such as REE^{3+} are adsorbed on the surface of oxides such as Fe- and/or Mn- oxides (hydroxides) due to decrease in electrostatic forces between them in solutions with pH values in a narrow interval close to pH_{PZC} (Parks, 1990; Davis and Kent, 1990). Previous works revealed that the pH_{PZC} values for solutions show variations as a function of temperature of solutions (Schoonen, 1994; Sverjensky, 1994). For examples, the studies conducted by Kosmulski (2006) showed that a temperature difference of 1°C can change the pH_{PZC} by up to about 0.03.

Many researchers have proposed mathematic/thermodynamic-based equations to calculate the values of pH_{PZC} for some minerals as a mineral-chemistry

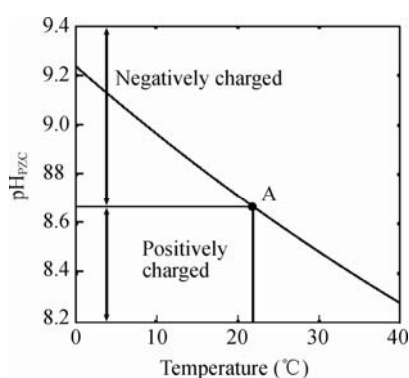


Fig. 7. Bivariate plot of temperature (in Celsius) versus pH_{PZC} for bauxite depositional conditions using equation (4).

The proposed temperature ($\sim 22^\circ\text{C}$) for bauxite depositional environment is from Bogatyrev and Zhukov (2009) and Mondillo et al. (2011).

characteristic (Schoonen, 1994; Sverjensky, 1994; Kosmulski, 2006). Based on experimental works done on various Fe and Al oxide minerals (e.g., magnetite, hematite, boehmite, and diasporite), the following equation was formulated to calculate the pH_{PZC} as a function of temperature (T) (Schoonen, 1994):

$$\text{pH}_{\text{PZC}} = 9.2433 - 0.02863 \times T + 0.000124 \times T^2 - 2.19 \times 10^{-7} \times T^3 \quad (4)$$

Figure 7 illustrates the bivariate plot of temperature ($^\circ\text{C}$) versus calculated pH_{PZC} using equation (4). Shown in this figure is the point A indicating the temperature of 22°C at which most bauxite deposits form, as proposed by Bogatyrev and Zhukov (2009) and Mondillo et al. (2011). At point (A) the pH_{PZC} value is 8.67 corresponding to zero charge. The pH values higher than 8.67 represent alkaline conditions and negatively charged surfaces for Fe-oxides, which are thought to be essential for scavenging REE^{3+} in the studied bauxite. Furthermore, the alkaline environment during formation of the RBRB part of the studied profile can be specified by the values of La/Y as a proxy for determination of alkaline-acidic environments (Crinci and Jurkovic, 1990; Maksimovic and Pantó, 1991). According to the calculated values of La/Y (see Table 2), the ratios in samples representing the RBRB part of the profile have values almost greater than 1 (average of 1.14) indicating an alkaline depositional environment for this part. The ratios in samples representing the upper parts of the profile (WPB and GCB) have values less than 1 (average of 0.77) testifying to acidic conditions during the development of these parts. These deductions are quite consistent with a strong positive correlation between Fe-oxides and REE values of the samples ($r=0.85$). It can be further deduced that the RBRB part of the bauxite horizon in this profile was probably developed at pH values greater than 8.67.

5.4 Occurrence of the tetrad effect

Certain irregular shapes in normalized REE distribution patterns known as the tetrad effect phenomenon have been reported from the Mortas-bauxite deposit of Turkey (Karadag et al., 2009) and the Kanigorgeh bauxite deposit of Iran (Abedini et al., 2018). Recent studies reveal that curves in normalized REE distribution patterns in various deposits worldwide are observed in three groups. The

curves of the first group display a convex form (M-like), and are generally observed in igneous or relevant evolved systems such as alteration, hydrothermal deposits, leucogranites, gneisses, granitoids, and pegmatites (Masuda et al., 1987; Masuda and Akagi, 1989; Lee et al., 1994; Kawabe, 1995; Peretyazhko and Savina, 2010; Ragab, 2011; Censi et al., 2016). The second group curves have a concave shape (W-like), and are characteristic of low-temperature seawater and marine deposits such as limestone, corals, phosphorites, underground waters, and cherts (Masuda et al., 1987; Lee et al., 1994; Akagi et al., 2004; Peretyazhko and Savina, 2010; Feng et al., 2014). The third group of curves have both convex and concave shapes, and represent certain types of deposits with different depositional histories such as the Tono Uranium deposit in Japan (Takahashi et al., 2002), volcanic glass (Takahashi et al., 2002), ferromanganese concretions and the Terra Rossa in China (Feng et al., 2011), glasses in porphyritic rocks of Ary-Bulak in Transbaikalia (Peretyazhko and Savina, 2010), cryolite from the Pitinga Mine in Brazil (Minuzzi et al., 2008), the Qahr-Abad fluorite deposit in Iran (Rezaei Azizi et al., 2017), the Dalir phosphatic shale in northern Iran (Abedini et al., 2017), and the Kanigorgeh titanium-rich bauxite deposit in Iran (Abedini et al., 2018).

Based on studies, it can be deduced that convex tetrad effect features or M-like shapes in chondrite-normalized REE distribution patterns are explained with the increase in the covalence number REE-O binding on the surface of solid materials or surface complexes (Censi et al., 2014), which can be related to decrease in the Racah parameter relative to aquatic-complex reactions (Censi et al., 2007). Moreover, these authors suggested that the occurrence of concave tetrad effect features or W-like shapes in chondrite-normalized REE distribution patterns are characteristic of solid-liquid heterogeneous interactions with a low covalent number of the REE-ligand complex.

Recently, some techniques have been proposed to quantify the magnitude of the tetrad effect phenomenon in normalized REE distribution patterns (e.g., Irber, 1999; Monecke et al., 2002). The individual tetrad groups in the normalized REE distribution pattern are labeled T_1 , T_2 , T_3 , and T_4 (or T_i), which are the magnitudes of first, second, third, and fourth tetrads, respectively. The size of T_i shows the magnitude of deviation for the second and third elements of each tetrad group from a straight line that connects the first and fourth elements to each other. This means that $T_i > 0$ is indicative of tetrad effect existence and $T_i = 0$ is indicative of non-tetrad effect phenomenon. In this paper, the size of the tetrad effect feature in each group of tetrads was calculated by the following equation (Monecke et al., 2002):

$$T_i = \sqrt{0.5 \times \left(\left[\frac{X_{Bi}}{\sqrt[3]{(X_{Ai}^2 \times X_{Di})}} - 1 \right]^2 + \left[\frac{X_{Ci}}{\sqrt[3]{(X_{Di}^2 \times X_{Ai})}} - 1 \right]^2 \right)} \quad (5)$$

In this equation, X is the concentration of elements. The A, B, C, and D represent the first, second, third, and fourth

elements of each tetrad group and index i is related to tetrad group. During quantification of the size of the tetrad effect, T_1 should be ignored in the case of Ce anomalous behavior (Monecke et al., 2002). Additionally, T_2 or the size of the second tetrad effect cannot be computed because of lack of Pm in the natural environment (McLennan, 1994).

The calculated values for the tetrad effect phenomenon using equation (5) in the first, third, and fourth tetrads of chondrite-normalized REE distribution patterns and the shape of normalized curves in these patterns for the bauxite samples in the studied profile are listed in Table 3. For clarification and better vision in variation of the tetrad

effect phenomenon in the samples from different parts of the studied profile, the chondrite-normalized REE patterns are illustrated in Fig. 8a-g. As listed in Table 3 and illustrated in Fig. 8a-g, the first tetrad (from B-1 to B-11 and from B-12 to B-21) displays convex (zigzag and/or M-like) and concave (zigzag and/or W-like) patterns, respectively. As illustrated in this figure, both concave (W-like) and convex (M-like) patterns are observed in the third and fourth tetrads. According to the previous studies and experiments carried out on the lanthanides reaction in aqueous systems (Masuda and Ikeuchi, 1979; Lee et al., 1994), the occurrence of zigzag pattern in normalized patterns are considered as a partial or incomplete tetrad

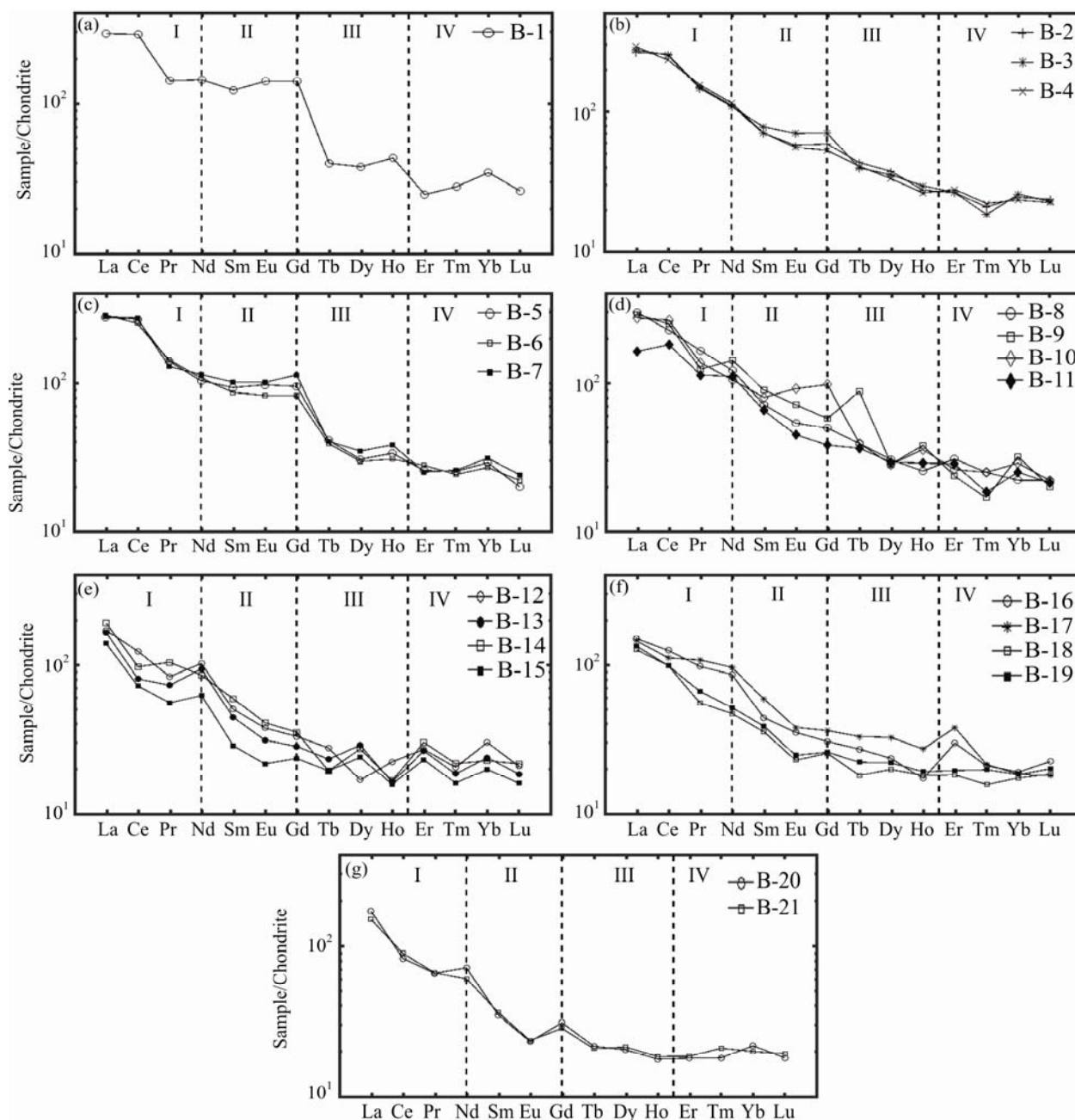


Fig. 8. Chondrite-normalized REE distribution patterns for the bauxite samples (a) B-1, (b) B-2, B-3, and B-4, (c) B-5, B-6, and B-7, (d) B-8, B-9, B-10, and B-11, (e) B-12, B-13, B-14, and B-15, (f) B-16, B-17, B-18, and B-19, and (g) B-20 and B-21. I, II, III, and IV indicate first, second, third, and fourth tetrad effect groups, respectively.

effect reaction between REE^{3+} and the ions in aqueous systems (Lee et al., 1994). The frequency diagrams of the computed T_3 (Fig. 9a) and T_4 (Fig. 9b) tetrad effect values in the bauxite samples indicate that the T_3 tetrad effect values have a conspicuous bimodal pattern. This means that two clusters of T_3 tetrad effect values with a similar range of variations and geological relationships (Alizadeh et al., 2012; Abedini et al., 2018) can be recognized in these samples (Fig. 9a). The first cluster includes bauxite samples from B-1 to B-10 with a median value equal to 0.3 for the T_3 tetrad effect; this group of bauxite samples indicates the alkalic zone (RBRB) of the studied horizon. The second cluster includes samples from B-11 to B-21 with a median value equal to 0.16 for T_3 tetrad effect. In contrast to the first cluster, the second cluster includes all bauxite samples which belong to the acidic parts (WPB and GCB) of the studied horizon. These clusters with diverse median values of T_3 tetrad effect in the bauxite

horizon can be attributed to different geochemical conditions of the depositional environment. Thus, the computed values of the T_3 tetrad effect in the studied bauxite samples proved to be a good indicator to assess the geochemical processes and the correlation between geochemical parameters and the T_3 tetrad effect.

5.5 Correlation between T_3 tetrad effect and geochemical indicators

During evolution of geochemical systems, some isoivalent pairs can be fractionated, which is useful as a geochemical indicator to evaluate the supergene and aquatic systems (Irber, 1999; Lawrence et al., 2006; Bau and Koschinsky, 2009; Tang et al., 2013; Gadd et al., 2016). Bau (1996) declared that distribution of isoivalent pairs such as Y-Ho and Zr-Hf are controlled by their CHARAC behavior in natural systems. Accordingly, fractionation of these elements can generate non-

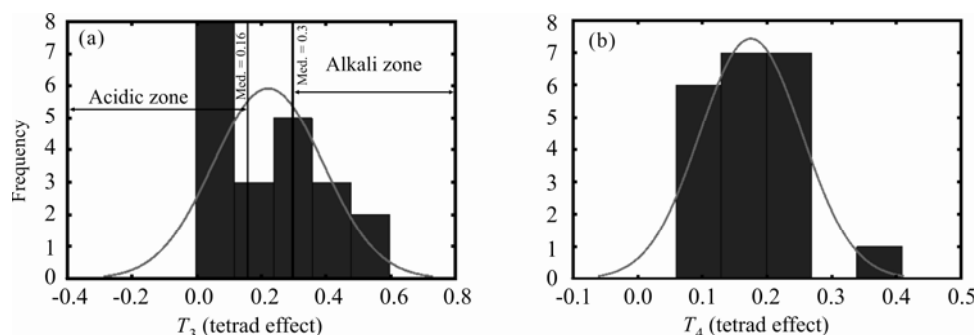


Fig. 9. Diagrams of frequency versus computed values for (a) T_3 tetrad effect and (b) T_4 tetrad effect in the bauxite samples.

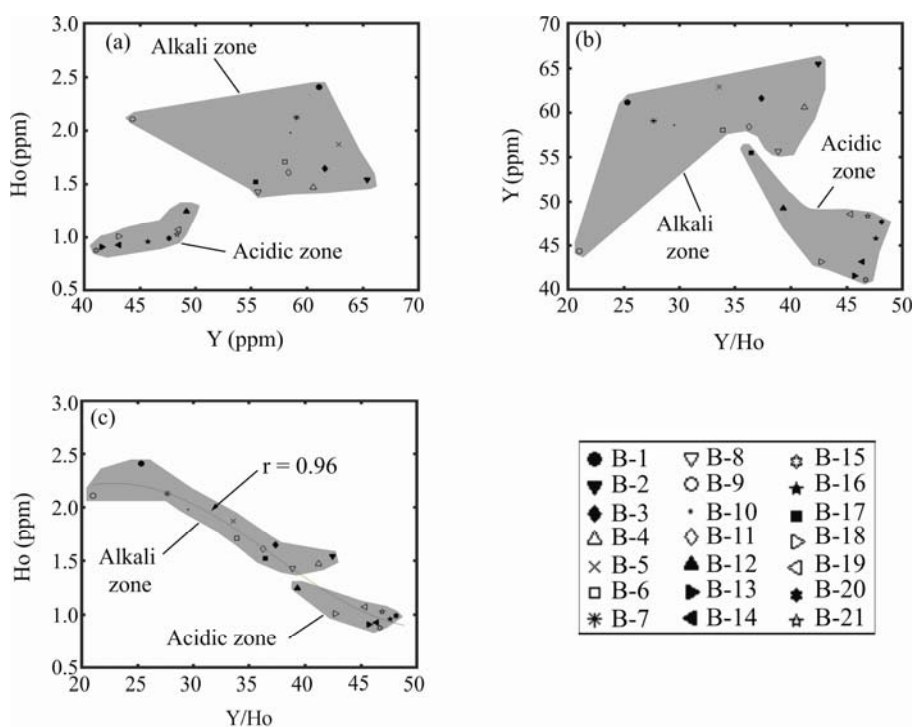


Fig. 10. Scatter plots of (a) Y (ppm) vs. Ho (ppm), (b) Y/Ho ratios vs. Y (ppm), and (c) Ho (ppm) vs. Y/Ho ratios.

The correlation curve between Ho and Y/Ho ratios of the bauxite samples in Fig. 10c was drawn by the following functional equation: $\text{Ho} = 1.55 - 0.55 \times \cos(0.11 \times \text{Y/Ho}) + 0.39 \times \sin(0.11 \times \text{Y/Ho})$.

Table 3 The size and shape (type) of curves in tetrad groups of the studied bauxite samples

Sample No.	First tetrad		Third tetrad		Fourth tetrad	
	Size	Type	Size	Type	Size	Type
B-1	0.24	Zigzag	0.50	W	0.25	M
B-2	0.21	M	0.06	M	0.13	W
B-3	0.18	M	0.19	W	0.20	W
B-4	0.07	M	0.02	W	0.10	W
B-5	0.25	Zigzag	0.37	W	0.24	M
B-6	0.16	Zigzag	0.32	W	0.10	M
B-7	0.25	Zigzag	0.43	W	0.19	M
B-8	0.02	M	0.04	M	0.09	W
B-9	0.23	M	0.59	M	0.40	Zigzag
B-10	0.24	M	0.44	M	0.16	M
B-11	0.20	M	0.06	M	0.21	W
B-12	0.24	W	0.24	W	0.26	M
B-13	0.38	W	0.33	M	0.18	M
B-14	0.24	W	0.28	Zigzag	0.14	W
B-15	0.32	W	0.24	M	0.17	M
B-16	0.04	Zigzag	0.11	M	0.23	W
B-17	0.09	W	0.06	M	0.24	W
B-18	0.12	W	0.14	W	0.11	W
B-19	0.04	W	0.05	W	0.06	W
B-20	0.33	W	0.12	W	0.15	M
B-21	0.19	W	0.11	W	0.09	M

CHARAC behavior due to the tetrad effect phenomenon (Bau, 1996; Veksler et al., 2005; Rezaei Azizi et al., 2017). The simultaneous occurrence of non-CHARAC characteristic and tetrad effect phenomenon in geochemical systems can be attributed to variation in depositional conditions and/or fluids/solutions (Minami et al., 1998). The latter authors suggested that Y-Ho fractionation in aqueous systems can be interpreted by convex and concave tetrad effect phenomena.

The correlation between Y and Ho (Fig. 10a) indicates that their fractionation has different trends in alkalic and acidic zones of the bauxite horizon. As shown in Figure 10a, the alkalic zone is characterized by low fractionation (with an average Y/Ho value of 33.14), whereas in the acidic part the Y/Ho ratios display more fractionation (with an average value of 43.83). As a result, it can be concluded that the Y/Ho ratios in the alkalic part of the profile are close to the chondritic value of 28 (Minami et al., 1998) but they show a noticeable increase in the acidic part. Mathematically, to clarify the correlation between the concentration of Y, Ho, and Y/Ho ratios, the scatter diagram of Y/Ho ratios of the bauxite samples versus Y concentrations (Fig. 10b) and Ho concentrations (Fig. 10c) are illustrated. As these figures display, there is not a meaningful correlation between Y/Ho ratios and Y (Fig.

10b); however, instead, there exists a good correlation ($r=0.96$) between Y/Ho ratios and Ho (Fig. 10c) indicating that Ho probably played an important role in the Y/Ho increment. This means that the Y/Ho ratios of the bauxite samples in the studied district strongly depend on Ho variations. Bau (1996) demonstrated that the higher values for the Y/Ho ratios are related to preferential scavenging of Ho by oxides, which is quietly consistent with the mathematical correlation results. The alkali part of the bauxite horizon is consistent with a very strong and positive correlation between the Fe-oxides and Σ REE in the studied bauxites (Fig. 6). A strong negative correlation ($r=0.96$) exists between the Y/Ho ratio and the T_3 tetrad effect values in the alkalic zone of the studied horizon (Fig. 11a), whereas there is no meaningful correlation between these two geochemical parameters in the acidic zones. This means that the tetrad effect phenomenon as a geochemical parameter controls the REE distribution (including Y) in the studied profile and therefore can be used as a good geochemical indicator to evaluate the processes in geochemical systems.

Previous studies have shown that pH of the environment is an important factor controlling REE distribution in bauxites (Karadag et al., 2009). In fact, solutions with low pH can remove REE from REE-bearing minerals in weathering conditions and precipitate these elements at higher pH in alkalic conditions (Henderson, 1984). As Fig. 12a illustrates, the diagram of Σ REE values versus the T_3 tetrad effect values indicates that the Σ REE values are separated into two groups. The first group belongs to samples from B-1 to B-10 with higher Σ REE values, and the second group represents samples with lower Σ REE values. Therefore, it can be concluded that the lower part of the horizon during geochemical processes has alkalic conditions, whereas the upper parts experienced low pH (acidic) conditions. These results are quite consistent with the Ce and Eu anomaly data. In addition, the acidic part of the studied horizon is characterized by low (LREE/HREE)_N values in contrast to the alkalic zone, which has remarkably higher (LREE/HREE)_N values (Fig. 12c).

Furthermore, bivariate plots of the T_3 tetrad effect values versus the ratios of La/Y (Fig. 12b) and (La/Yb)_N (Fig. 12d) for all bauxite samples demonstrate two separate domains as well. As shown in the Fig. 12b, the La/Y values, as an indicator of acidity-alkalinity, display two separate populations. The first population has higher La/Y values (>1), being indicative of alkalic conditions. The second one has relatively lower La/Y values (<1), and

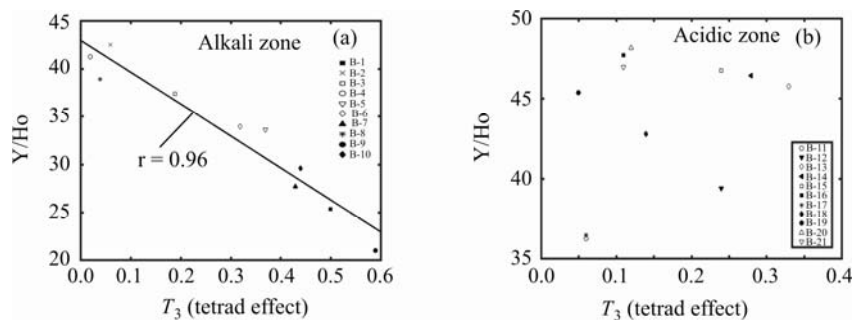


Fig. 11. Scatter plots of T_3 tetrad effect vs. Y/Ho ratios for (a) alkali zone, (b) acidic zone. The correlation line between T_3 tetrad effect and Y/Ho ratios of the bauxite samples in the alkali zone is defined as: $Y/Ho = -33.29 \times T_3 + 43$.

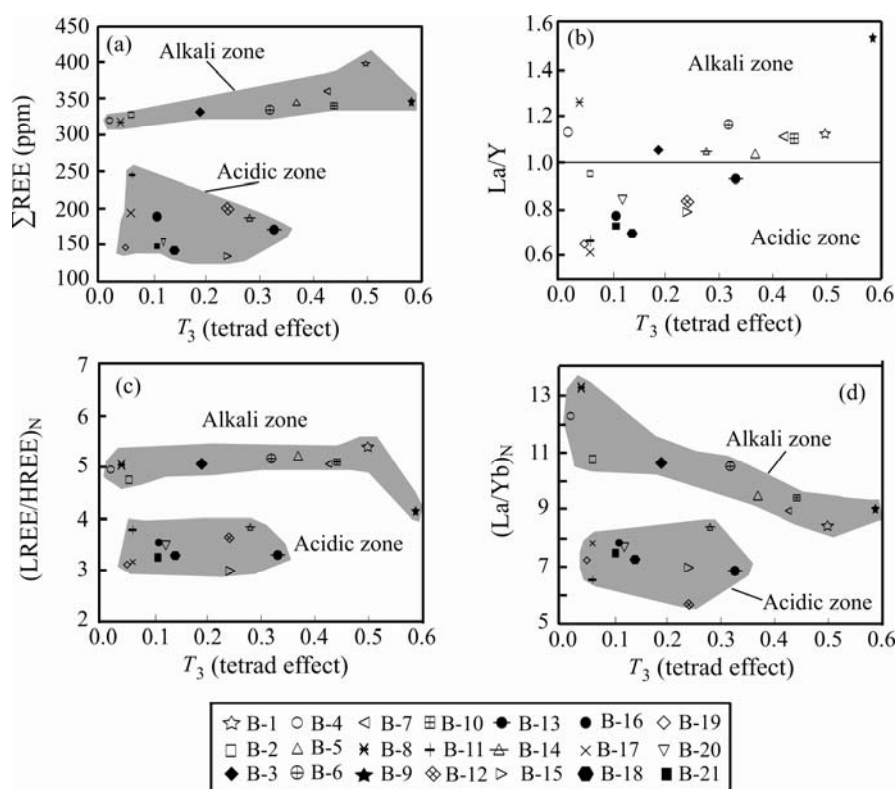


Fig. 12. Scatter plots of T_3 tetrad effect versus (a) ΣREE (ppm), (b) La/Y , (c) $(\text{LREE}/\text{HREE})_N$, and (d) $(\text{La}/\text{Yb})_N$ values for the bauxite samples in the studied district.

can be attributed to acidic conditions (Crinci and Jurkovic, 1990; Maksimovic and Pantó, 1991). Meanwhile, the $(\text{La}/\text{Yb})_N$ ratios as a geochemical factor can be used to evaluate the acidic-alkalic conditions of the depositional environments (Abedini et al., 2018). On the other hand, occurrence of the tetrad effect in normalized REE distribution patterns can be due to the presence of various ligands in aqueous systems and the stability of the REE-complexing (Feng et al., 2014; Rezaei Azizi et al., 2017). This means that interaction of acidic solutions with carbonate host rocks caused the solution to gain higher pH and then facilitate the precipitation of REE-bearing minerals. This can conceivably account for the ΣREE increase in the residual products. This conclusion is quite consistent with the nature of solution-rock interaction, which is characterized by the existence of simultaneous concave and convex tetrad effect values in the geochemical systems (Kawabe et al., 1999; Abedini et al., 2018). Consequently, it can be deduced that the acidic zone of the bauxite horizon has low T_3 tetrad effect values and $(\text{La}/\text{Yb})_N$ ratios, but the alkalic zone is characterized by higher $(\text{La}/\text{Yb})_N$ ratios. Based on present data, it can be concluded that tetrad effect values can be used as an important and useful indicator to assess the geochemical processes and depositional conditions during bauxitization.

5.6 Correlation between T_3 tetrad effect and major elements

The scatter diagram of $\text{Al}_2\text{O}_3 + \text{LOI}/\text{SiO}_2 + \text{Fe}_2\text{O}_3$ versus T_3 tetrad effect values (Fig. 13a) of the bauxite samples

indicates that variation of the T_3 tetrad effect values is related to intensity of bauxitization, desilicification, and deferruginization-ferruginization mechanisms. As shown in Fig. 13b, the existence of two separate populations indicates that the fractionation of Al from Fe in the bauxite samples has likely played an important role for the variation of T_3 tetrad effect values. The bivariate plot of $\text{Al}_2\text{O}_3 + \text{LOI}$ versus values of T_3 tetrad effect also displays two separate groups of samples (Fig. 13c). This implicates that the intensity of bauxitization might have played a key role during the evolution of the studied horizon. The diagram of T_3 tetrad effect values versus $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ (Fig. 13d) delineates that desilicification-silicification processes and simultaneous deferruginization and ferruginization are likely other important factors controlling the geochemical processes in the studied horizon. Finally, the T_3 tetrad effect values as a geochemical indicator can separate the IOL values of the acidic and alkali zones (Fig. 13e). This signifies that the T_3 tetrad effect values depend largely on lateritization intensity.

6 Conclusions

Based on data obtained from chemical analyses, REE distribution patterns, the pH_{PZC} , and tetrad effect values in the collected bauxite samples from different parts of the bauxite horizon in the Shahindezh district, NW Iran, the following conclusions can be drawn:

The meaningful and positive correlation ($r=0.85$) between the Fe-oxides values and ΣREE in the studied

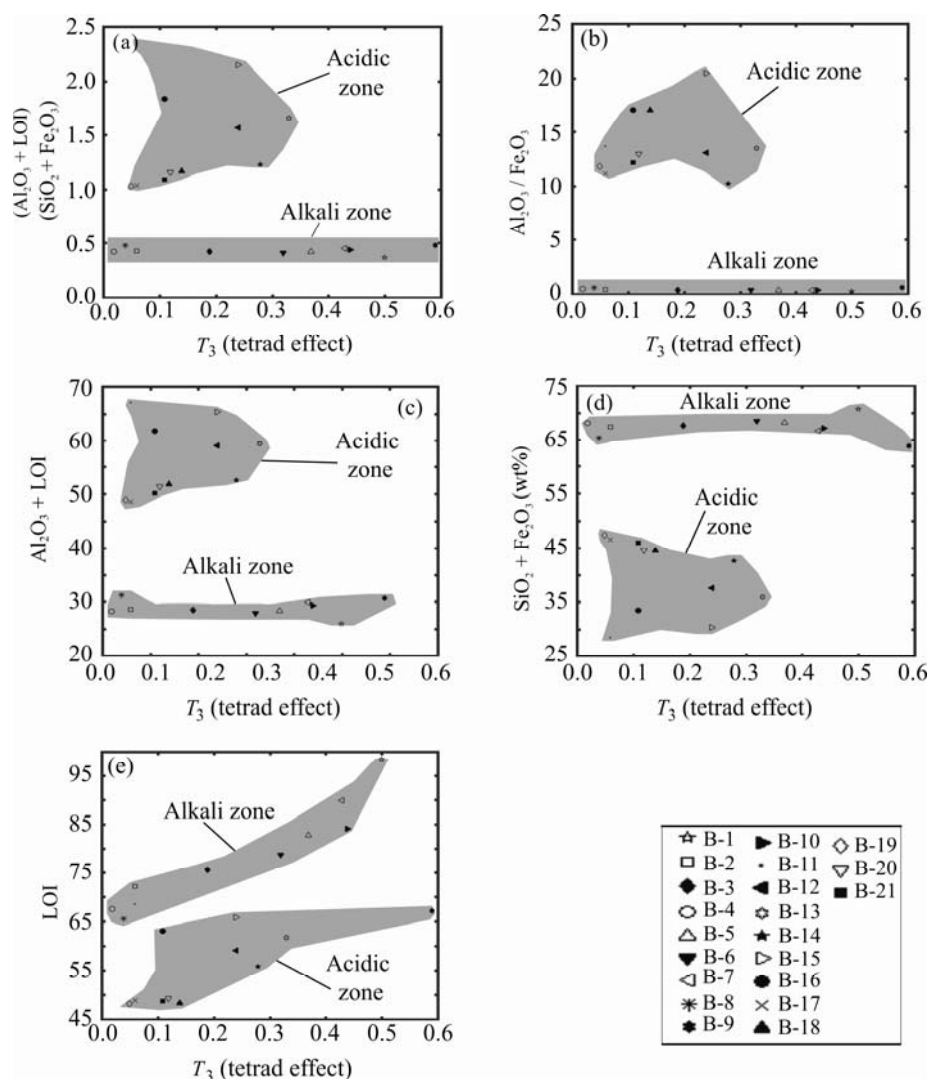


Fig. 13. Bivariate diagrams of T_3 tetrad effect values versus (a) $(\text{Al}_2\text{O}_3 + \text{LOI})/(\text{SiO}_2 + \text{Fe}_2\text{O}_3)$, (b) $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$, (c) $\text{Al}_2\text{O}_3 + \text{LOI}$, (d) $\text{SiO}_2 + \text{Fe}_2\text{O}_3$, and (e) IOL values in the bauxite samples of the Shahindezh bauxite horizon.

samples indicates that Fe-oxides are likely the main scavengers for fixing the REE in the lower part (RBRB) of the bauxite horizon. Moreover, the existence of irregular shapes of the chondrite-normalized REE patterns and non-CHARAC behavior of certain trace elements (e.g., Y/Ho ratios) can be affiliated to the occurrence of tetrad effect phenomenon in the studied samples;

Combining the point of zero charge (PZC) as a geochemical factor with other geochemical parameters like Ce and Eu anomalies led us to infer that the pH_{PZC} of the lower part of the studied horizon was ≥ 8.67 ;

The co-occurrence of convex and concave tetrad effects in the normalized REE distribution patterns can be attributed to variation in geochemical parameters and/or conditions during deposition of the bauxite horizon;

The bivariate diagrams of T_3 tetrad effect values versus Y/Ho, ΣREE , La/Y, $(\text{La}/\text{Yb})_N$, $(\text{LREE}/\text{HREE})_N$, $\text{Al}_2\text{O}_3 + \text{LOI}/\text{SiO}_2 + \text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3 + \text{LOI}$, IOL, and $\text{SiO}_2 + \text{Fe}_2\text{O}_3$ indicate that the studied bauxite horizon was deposited under two different geochemical conditions.

Thus, the tetrad effect values can be used as an effective indicator to evaluate the geochemical processes during formation and evolution of bauxite deposits;

Based on the above, it can be deduced that the occurrence of the T_3 tetrad effect in the studied horizon is likely related to the pH variation of the solutions during bauxitization of the parent rocks. In other words, the pH variations in the depositional environment had a key role in the development of the bauxite horizon.

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