

Rare Earth Elements Geochemistry of Sheikh-Marut Laterite Deposit, NW Mahabad, West-Azarbaidjan Province, Iran

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Abstract: Laterite deposit at Sheikh-Marut (NW Mahabad, West-Azarbaidjan province, Iran) occurred within middle–upper Permian carbonate rocks. It consists of seven stratiform and/or discontinuous lenticular layers extending over 4.2 km in length and having thicknesses ranging from 3 to 14 m. Mineralogical data show that the ores contain kaolinite and hematite as major and boehmite, diaspore, halloysite, amesite, anatase, and muscovite-illite as minor mineral phases. The computed Ce anomaly values in the ores range from 0.05 to 20.84. Conservative index (e.g., Eu/Eu^*) suggests that this deposit is a product of alteration and weathering of basaltic rocks. Rhythmic increment of ΣREE values of the ores with approaching to the carbonate bedrocks shows an in-situ occurrence of lateritization processes. Mass change calculations of elements indicate that two competing processes namely leaching and fixation were the major regulating factors in concentration variation of REEs (La–Lu) in this deposit. The obtained results show that pH increase of weathering solutions by carbonate bedrocks, existence of organic matters, and the degree of complexation with organic ligands played remarkable role in distribution of REEs during lateritization. Further geochemical considerations revealed that secondary phosphates, Mn-oxides and -hydroxides, diaspore, and anatase were the potential hosts for REEs in this deposit.

Key words: laterite, geochemistry, REEs, Sheikh-Marut deposit, Mahabad, Iran

1 Introduction

Laterite (means brick or tile in Latin) is a residual rock formed by the function of chemical weathering processes in tropical and semi-tropical regions (Mohamed El-Ahmady, 2010). Progression of lateritization processes can lead to the formation of bauxitic ores that could be economically very important in light of containing elements such as Al, Ga, and REEs (Calagari and Abedini, 2007; Liu et al., 2010). During past three decades, lateritic deposits in different parts of the world were studied in detail for realization of factors related to mobilization, differentiation, and redistribution of REEs during weathering processes (Braun et al., 1990; Nesbitt and Wilson, 1992; Oliva et al., 1999; Patino et al., 2003; Ma et al., 2007; Yang, 2008; Yang et al., 2008; Sanematsu et al., 2011). These studies revealed that factors such as pH, Eh, presence of organic and inorganic complexing ligands, adsorption, scavenging, degree of stability of carrier minerals against weathering, and fixation in neomorph

phases played very crucial role in behavior and distribution of REEs during lateritization processes. Further work, however, implemented by Yang et al. (2008) led to the exploration of a new type of REE deposits in basalt-derived laterites. In Iran, there are many lateritic deposits belonging mainly to Permian period and chiefly were developed within carbonate rocks. These deposits often contain bauxite and kaolinite ores. No comprehensive studies have been done so far on factors influencing upon distribution of REEs in ores of this type of deposits in Iran. In this study, Sheikh-Marut lateritic deposit (located in 15 km of NW Mahabad, West-Azarbaidjan province, NW Iran) as a typical example of this type of deposits was chosen and the controlling factors on distribution of REEs in the ores were considered in detail.

2 Geology

2.1 Geologic setting

The studied bauxitic deposit is part of the Sanandaj-

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Sirjan structural zone (Fig. 1a). The Permian limestones in this area experienced several depositional cessations by epirogenic movements during upper Permian (Kamineni and Eftekhhar-nezad, 1977). The entire Iranian platform was affected by these movements that were accompanied locally by basic volcanic activities especially in Alborz mountain chain. These eruptive basic volcanic rocks are cropped out in many locations in northwest of Iran (Kamineni and Eftekhhar-nezad, 1977; Calagari and Abedini, 2007) including in the study area. As a result of upper Permian epirogenic movements, major uplift took place which was followed by marine regression from a vast region along NW–SE trending belt in Iran. Lateritization occurred after each uplift event that was repeated several times during the formation of Permian limestones.

During late Triassic to early Jurassic time the Paleozoic platform in the west of Iran (separated structurally from the central Iranian platform) sank and a deep trough was developed, which was filled by thick Jurassic–Cretaceous sediments. These sediments are present in NW Iran (Kamineni and Eftekhhar-nezad, 1977). During Laramide movements the Sanandaj–Sirjan structural zone was established and the rocks underwent strong deformation and/or regional metamorphism, accompanied by magmatism (Kamineni and Eftekhhar-nezad, 1977). These geologic events are believed to have affected the laterites. Some of these laterites, however, due to bauxitization and kaolinization processes were partially converted into bauxite and kaolin.

2.2 Geology of the deposit

Based on depositional characteristics of residual deposits throughout the world (Bardossy, 1982), the lateritic deposit of Sheikh-Marut is reckoned to be a part of Irano-Himalayan karst bauxite belt. Cambrian sandstone (Lalun Formation) along with Cambro-Ordovician cherty dolomite and limestone (Mila Formation) are the oldest sedimentary formations in Sheikh-Marut region. In this region, sediments belonging to Devonian, Carboniferous, and lower Permian do not crop out. Middle–upper Permian carbonate rocks (Ruteh Formation), Cretaceous volcanics, carbonates, shales, and sandstones, along with Miocene limestone (Qom Formation), and recent (Quaternary) sediments are the stratigraphic sequence of the region (Fig. 1b). The conspicuous geologic aspect of Sheikh-Marut area is the repeated depositional cessations within the upper Permian period, which can be inferred by the development of horizons of lateritic ores within the carbonate rocks.

Sheikh-Marut lateritic deposit consists of seven discontinuous lateritic layers and/or lenses (Fig. 1b)

having two overall trends NE–SW and N–S extending over 4.2 km with varying thicknesses ranging from 3 to 14 m. On surface outcrops, the ores have different colors (red, dark red, brick-red, and brownish red). The function of kaolinization and bauxitization processes in some layers caused the partial development of kaolin and bauxite (particularly in the upper parts of the horizon) exhibiting a spectrum of colors from green through cream to gray. In most places at the lower contact zone, because of gradual percolation of Fe-bearing solutions into the existence fractures and joints of the bedrocks the carbonates turned into pink and purple colors. Limonitization, development of cataclastic textures in faulted zones, and the existing of sharp boundaries between the ores and enclosing rocks are noticeable geologic features in this deposit. In places, along the lower contact of the lateritic ores with bedrocks there are remains of irregular patches of relatively altered basaltic rocks within the carbonates. A close examination of textural features and colors of the ores across one of the selected lateritic layer led us to recognize four distinct lateritic facies that are, from bottom to the top, (1) dark red laterite, (2) brownish red laterite, (3) red laterite, and (4) brick-red laterite (Fig. 2). The two lower units (i.e., dark red and brownish red laterites) exhibit massive structure while the upper two units (i.e., red and brick-red laterites) are layered. The massive ores relative to layered ones are much denser. The significant physical characteristics of studied profile include development of pelitomorphic textures, dendritic manganese aggregates, and micro-veinlets of micaceous hematite in the red and brick-red ores, and presence of concretionary textures (nodular, ooidic, and pisoidic) in the dark red and brownish red ores. Red and red-brick ores have soapy, greasy, and earthy aggregates while dark red and brownish red ores are hard with conchoidal fracture surfaces.

3 Sampling and Analytic Methods

Field works began with a selected traverse perpendicular to the strike of the lateritic layer (8 m thickness). Fifteen ore samples (with an interval of about 0.5 meter from bedrock toward the cap rocks) along with three rock samples from existing basaltic patches at the contact zone, and two rock samples from carbonate bedrocks were taken. After preparation, the samples were analyzed for major and trace elements (using ICP-ES method) and for REEs (using ICP-MS method) at ACME Laboratories in Canada. Loss on ignition (LOI) was measured by weighing the samples before and after 1 hour of heating at 1000°C. The analysis results are listed in Tables 1 and 2. For determination of mineralogical compositions of the deposit, eight alternate samples were

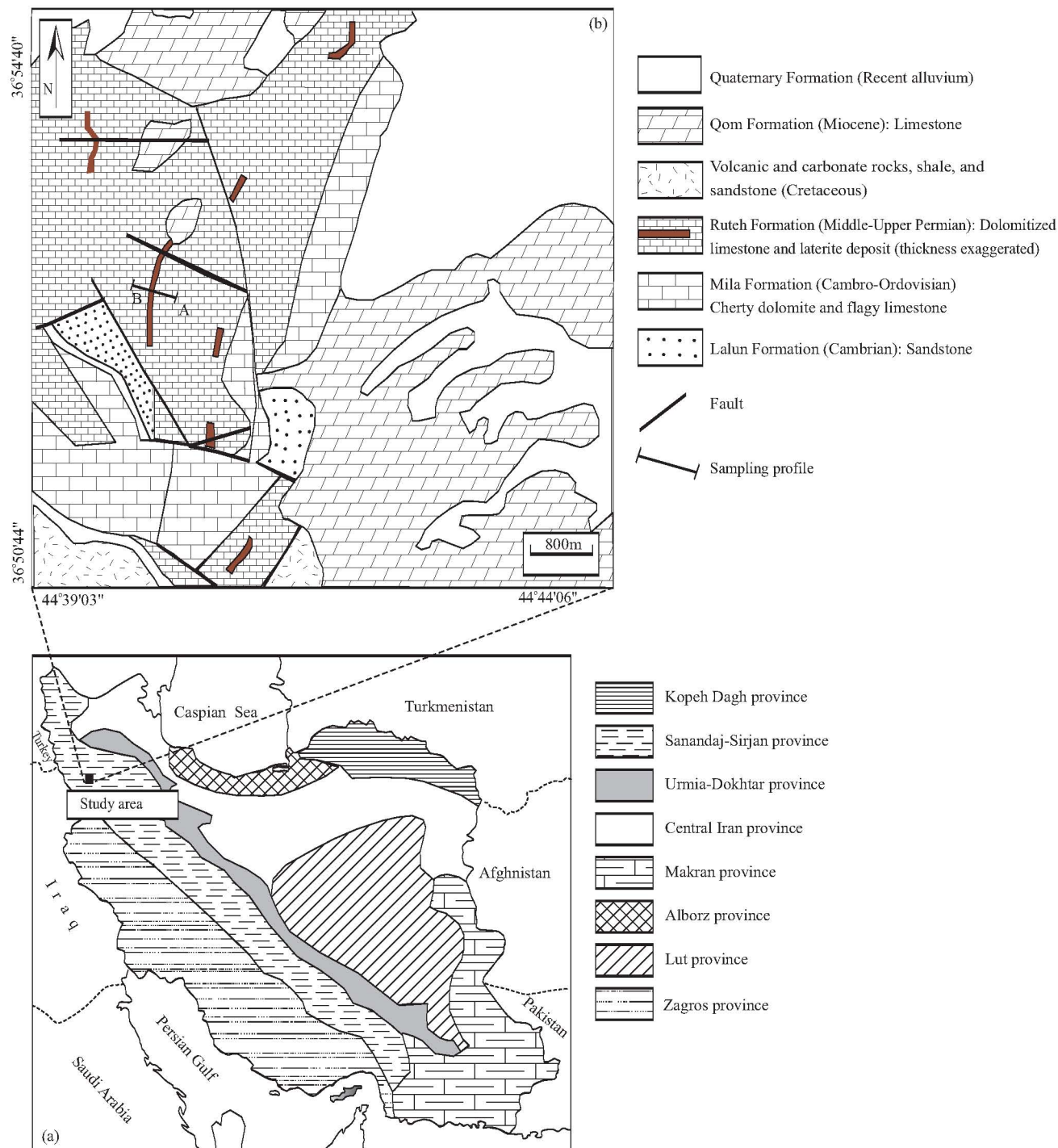


Fig. 1. (a) General map of Iran showing all the eight structural zones. The study area is located in the Sanandaj-Sirjan structural zone (modified after Vaziri-Moghaddam et al., 2006; Khanehbad et al., 2012). (b) A Geologic map illustrating the position of laterite layers and/or lenses at Sheikh-Marut.

also selected for XRD analyses done at Geological Survey of Iran (using Model D-5000 SIMENS diffractometer with CuK α radiation, fixed graphite chromators, voltage 40 kV, current 40 mA, scanning speed 2° per minute, scan range 2–70°, and drive axis 2 θ). In this study, for consideration of elemental relations and better geochemical interpretation attempts have been made to calculate the

Pearson correlation coefficients among elements by using software package SPSS version 16.

4 Results

4.1 Mineralogical examinations

XRD analyses revealed that the lateritic ores have

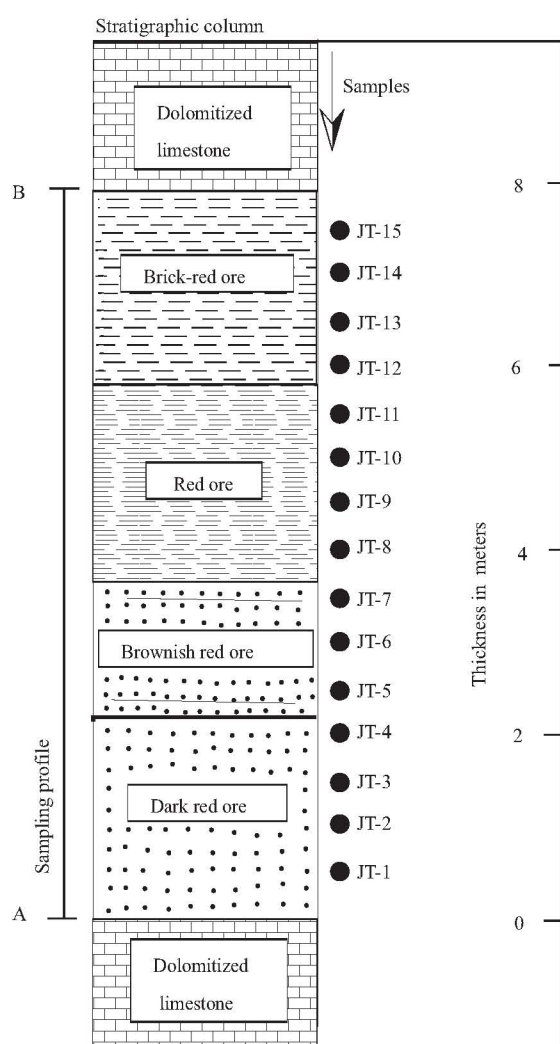


Fig. 2. A stratigraphic column across the selected Permian lateritic layer at Sheikh-Marut (for position see Fig. 1b) along with the location of analyzed samples.

relatively simple mineralogy. Kaolinite and hematite (as major mineral phases) are accompanied by lesser amounts of boehmite, diasporite, halloysite, amesite, anatase, and muscovite-illite (as minor mineral phases) in the ores.

4.2 Geochemical investigations

4.2.1 Distribution trend of major and trace elements in the deposit

Chemical analyses illustrate that major components of the lateritic ores are Fe_2O_3 (9.57–24.25 wt%), Al_2O_3 (9.81–40.17 wt%), SiO_2 (25.23–59.95 wt%), TiO_2 (1.59–4.92 wt%), and LOI (8.92–18.59 wt%) (Table 1). These components display a wide range of variations. Alkaline and earth alkaline elements along with P and Mn (in oxide forms) exist in very low values making up altogether 1.14–2.12 wt% of the ores. The most significant elemental relationships are moderate to good correlations among pairs of Al_2O_3 – Fe_2O_3 ($r=0.65$), TiO_2 – Al_2O_3 ($r=0.88$), TiO_2 – Fe_2O_3 ($r=0.86$), and Al_2O_3 – MgO ($r=0.73$); and good but negative correlations among pairs of Al_2O_3 – SiO_2 ($r=-0.92$) and SiO_2 – Fe_2O_3 ($r=-0.87$). Regarding the results of chemical analyses, immobile elements in order of increasing abundance such as Th (in values <10 ppm), Y, Nb, and Sc (in values ~10 ppm), and Zr (in values ranging from 10 to 100 ppm) are present in the ores. Among these elements, Sc (with values ranging from 33 to 37 ppm) suffered the least variations during lateritization processes (see Table 1). Correlation coefficient values show that TiO_2 has very good and positive correlation ($r=0.98$ – 0.99) with Nb, Y, and Th suggesting their similar geochemical behavior during lateritization.

4.2.2 Distribution trend of REEs in the deposit

With referring to the results of chemical analyses (see

Table 1 Analytic results of major oxides and LOI (in wt%) and selective trace elements (in ppm) in the lateritic ores, basaltic rocks, and carbonate bedrocks at Sheikh-Marut.

	Rock type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Cr_2O_3	LOI	Zr	Th	Y	Sc	Nb
LS-1	Carbonate	16.84	5.53	2.69	40.87	0.81	0.08	0.96	0.11	0.04	0.07	0.008	31.93	11.3	2.3	5.8	2.5	1.9
LS-2	Carbonate	15.75	2.76	1.39	42.93	0.83	0.03	0.27	0.08	0.04	0.04	0.009	35.75	15.8	2.2	4.2	2.8	2.1
HS-1	Basalt	47.61	16.12	15.71	6.62	6.09	2.73	1.11	2.05	0.29	0.96	0.048	0.37	124.1	2.5	29.5	33.0	23.4
HS-2	Basalt	47.24	15.51	15.42	8.06	6.61	2.41	0.82	2.09	0.24	0.99	0.044	0.56	137.2	2.3	28.9	33.0	26.2
HS-3	Basalt	46.82	14.94	16.44	6.84	7.52	2.93	0.81	2.04	0.16	0.97	0.047	0.39	114.3	2.4	27.7	32.0	27.8
JT-1	Laterite	30.12	29.74	21.81	0.01	0.63	0.03	0.44	3.76	0.36	0.65	0.051	12.21	219.2	5.1	29.4	35.0	35.8
JT-2	Laterite	25.23	40.17	19.72	0.01	0.51	0.07	0.02	4.92	0.34	0.53	0.052	8.42	299.4	6.1	28.4	37.0	48.1
JT-3	Laterite	26.54	34.97	20.34	0.01	0.46	0.07	0.04	4.51	0.34	0.32	0.054	12.29	281.3	5.8	25.8	37.0	44.9
JT-4	Laterite	27.97	29.84	20.94	0.01	0.42	0.06	0.05	4.01	0.31	0.29	0.056	15.95	264.7	5.5	25.1	35.0	41.6
JT-5	Laterite	28.48	28.41	23.47	0.02	0.36	0.04	0.61	3.89	0.29	0.23	0.063	13.97	248.9	4.9	29.8	35.0	38.4
JT-6	Laterite	26.49	28.2	24.35	0.02	0.29	0.07	0.56	4.19	0.3	0.21	0.064	15.21	278.6	4.9	25.7	35.0	40.6
JT-7	Laterite	25.84	32.21	20.31	0.02	0.59	0.06	0.06	4.72	0.33	0.31	0.056	15.24	281.2	6.1	28.4	35.0	48.2
JT-8	Laterite	41.95	12.67	23.43	0.01	0.65	0.12	0.05	4.07	0.23	0.18	0.057	16.16	232.1	5.2	33.2	34.0	35.5
JT-9	Laterite	51.63	10.96	15.71	0.01	0.59	0.11	0.19	1.78	0.26	0.25	0.051	18.15	84.3	1.8	26.5	33.0	18.9
JT-10	Laterite	55.62	9.81	13.77	0.01	0.48	0.11	0.03	1.6	0.31	0.26	0.043	17.64	67.6	1.8	23.3	33.0	17.2
JT-11	Laterite	49.62	11.41	16.91	0.01	0.63	0.09	0.27	1.98	0.25	0.27	0.041	18.21	83.3	1.9	21.4	34.0	19.7
JT-12	Laterite	58.67	15.34	9.74	0.01	0.85	0.03	0.23	1.59	0.26	0.25	0.043	12.68	73.4	1.7	17.6	34.0	13.6
JT-13	Laterite	59.95	12.72	9.57	0.02	0.87	0.14	0.03	1.57	0.28	0.23	0.042	14.14	74.2	1.9	20.1	33.0	17.9
JT-14	Laterite	54.66	11.54	13.71	0.02	0.77	0.11	0.21	1.75	0.3	0.28	0.047	16.25	79.3	1.1	16.5	33.0	18.7
JT-15	Laterite	53.95	11.94	11.67	0.01	0.66	0.07	0.33	1.72	0.26	0.18	0.046	18.59	74.3	1.7	21.5	34.0	20.5

Table 2 Analytic results for REEs in the lateritic ores, basaltic rocks, and carbonate bedrocks (in ppm) at Sheikh-Marut

	Rock type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LS-1	Carbonate	34.30	63.30	7.46	26.30	3.81	0.33	2.96	0.37	1.78	0.22	0.76	0.09	0.56	0.07
LS-2	Carbonate	25.20	47.8	5.64	19.80	2.81	0.21	2.13	0.26	1.25	0.14	0.53	0.06	0.38	0.06
HS-1	Basalt	26.60	32.90	4.02	16.70	3.88	1.19	4.88	2.82	2.21	5.76	3.95	2.85	3.78	2.71
HS-2	Basalt	26.30	28.20	3.23	16.50	4.36	1.26	4.75	2.74	2.11	5.82	3.98	2.94	4.03	2.75
HS-3	Basalt	24.20	29.5	3.91	16.50	5.92	1.42	4.35	2.78	2.12	5.79	3.94	2.72	3.84	2.79
JT-1	Laterite	126.52	2074.00	31.36	56.45	15.91	4.55	17.64	7.01	9.28	5.88	4.23	2.55	2.00	2.41
JT-2	Laterite	34.56	1731.00	11.14	41.47	13.59	4.66	20.92	7.92	9.41	6.56	4.35	2.95	3.72	2.55
JT-3	Laterite	33.84	1039.00	9.82	35.71	11.03	3.51	14.55	6.22	7.63	5.16	3.51	2.41	2.62	1.95
JT-4	Laterite	32.88	334.00	8.48	29.57	8.45	2.26	8.17	4.45	5.83	3.88	2.67	1.71	3.58	1.65
JT-5	Laterite	34.08	300.00	7.36	25.63	6.82	1.81	6.35	3.32	4.57	2.92	2.14	1.41	3.50	1.35
JT-6	Laterite	27.96	150.10	5.39	16.80	4.33	1.10	3.67	1.95	2.89	2.45	1.31	0.84	1.15	0.85
JT-7	Laterite	33.84	566.00	10.33	41.57	13.09	3.34	11.17	6.61	8.75	5.81	3.89	2.71	3.50	2.31
JT-8	Laterite	5.81	1.44	5.22	4.68	1.41	0.28	0.50	0.66	0.55	0.41	0.42	0.34	0.40	0.47
JT-9	Laterite	12.99	8.65	11.71	10.12	2.95	0.60	1.05	1.37	1.25	0.68	0.55	0.28	0.51	0.43
JT-10	Laterite	14.56	9.66	12.79	11.24	3.41	0.55	1.20	1.53	1.35	0.76	0.65	0.27	0.55	0.48
JT-11	Laterite	12.22	5.99	11.15	6.28	2.01	0.39	1.01	1.28	1.15	0.64	0.51	0.33	0.51	0.47
JT-12	Laterite	13.37	11.59	6.10	5.56	2.05	0.29	0.29	0.74	0.65	0.46	0.45	0.41	0.40	0.37
JT-13	Laterite	17.99	7.07	14.74	14.04	4.71	0.82	1.95	2.49	2.20	1.19	0.50	0.29	0.75	0.63
JT-14	Laterite	14.88	5.22	12.90	11.80	3.65	0.63	1.45	1.93	1.65	0.96	0.35	0.29	0.80	0.67
JT-15	Laterite	11.41	3.19	10.82	9.52	2.65	0.34	0.55	1.20	0.41	0.60	0.50	0.38	0.45	0.38

Table 3 Ratio of REEs in the lateritic ores, basaltic rocks, and carbonate bedrocks at Sheikh-Marut

	Rock type	$\Sigma\text{LREE}_{\text{La-Gd}}$	$\Sigma\text{HREE}_{\text{Tb-Lu}}$	ΣREE	La/Y	La/Yb	$\Sigma\text{LREE}/\Sigma\text{HREE}$	Eu/Eu*	Ce/Ce*
LS-1	Carbonate	138.46	3.85	142.31	5.91	381.11	35.96	0.47	0.90
LS-2	Carbonate	103.59	2.68	106.27	6.00	420.00	38.65	0.41	0.92
HS-1	Basalt	90.17	24.08	114.25	0.90	9.82	3.74	0.81	0.72
HS-2	Basalt	84.6	24.37	108.97	0.91	9.56	3.47	0.82	0.62
HS-3	Basalt	85.8	23.98	109.78	0.87	8.67	3.58	0.83	0.66
JT-1	Laterite	2326.43	33.36	2359.79	4.30	52.50	69.74	0.81	7.63
JT-2	Laterite	1857.34	37.46	1894.80	1.22	13.55	49.58	0.82	20.84
JT-3	Laterite	1147.46	29.5	1176.96	1.31	17.35	38.90	0.82	13.40
JT-4	Laterite	423.81	23.77	447.58	1.31	19.93	17.83	0.81	4.66
JT-5	Laterite	382.05	19.21	401.26	1.14	25.24	19.89	0.81	4.32
JT-6	Laterite	209.35	11.44	220.79	1.09	32.89	18.30	0.82	2.74
JT-7	Laterite	679.34	33.58	712.92	1.19	14.65	20.23	0.82	7.13
JT-8	Laterite	19.34	3.25	22.59	0.18	12.36	5.95	0.82	0.06
JT-9	Laterite	48.07	5.07	53.14	0.49	30.21	9.48	0.81	0.15
JT-10	Laterite	53.41	5.59	59.00	0.62	30.33	9.55	0.81	0.15
JT-11	Laterite	39.05	4.89	43.94	0.57	26.00	7.99	0.82	0.11
JT-12	Laterite	39.25	3.48	42.73	0.76	36.14	11.28	0.82	0.15
JT-13	Laterite	61.32	8.05	69.37	0.90	28.56	7.62	0.81	0.05
JT-14	Laterite	50.53	6.65	57.18	0.90	22.21	7.60	0.82	0.08
JT-15	Laterite	38.48	3.92	42.40	0.53	30.03	9.82	0.81	0.06

Table 2), the anomalous levels of the lateritic ores are $\Sigma\text{REE}=22.59\text{--}2359.79$ ppm, $\Sigma\text{LREE}=19.34\text{--}2326.43$ ppm, $\Sigma\text{HREE}=3.92\text{--}37.46$ ppm, $\text{La/Y}=0.18\text{--}4.30$, $\text{La/Yb}=14.65\text{--}52.30$, $\Sigma\text{LREE}/\Sigma\text{HREE}=5.95\text{--}69.74$ (see Table 3). Anomalies of Eu and Ce were calculated by using equations $\text{Eu}/\text{Eu}^*=\text{Eu}_N/(\sqrt{\text{Sm}_N \times \text{Gd}_N})$ and $\text{Ce}/\text{Ce}^*=2\text{Ce}_N/(\text{La}_N+\text{Pr}_N)$ (Taylor and McLennan, 1985) (where N stands for normalization to chondrite). The anomalous values of Eu vary from 0.81 to 0.82 (with an average of 0.815) and of Ce from 0.05 to 20.84 (with a mean of 4.09). The pronounced points concerning variation mode of anomalous levels are the irregular increase in values of ΣREE (Fig. 3a), ΣLREE (Fig. 3b), ΣHREE (Fig. 3c), $\Sigma\text{LREE}/\Sigma\text{HREE}$ (Fig. 3d), and La/Y (Fig. 3e) downward from top toward the carbonate bedrocks, and also the inharmonious distribution of La/Yb (Fig. 3f) in the profile. The variation mode of Ce/Ce^* ratio is the irregular increase downward from top toward the carbonate

bedrocks (Fig. 3g). Variation in the Eu/Eu^* ratio is very minor (Fig. 3h).

4.2.3 Parental affinity

Distribution pattern of REEs particularly anomaly values of Eu in weathered materials and residual ores are accepted as important markers for determination of protolith of the lateritic ores (Schellmann, 1986; Mongelli, 1997; Nyakairu and Koeberl, 2001; Mameli et al., 2007; Muzaffer-Karadağ et al., 2009). Normally, weathering brings about weak differentiation between LREEs and HREEs along with poor negative and/or no anomaly of Eu in basic igneous rocks during weathering. On the other hand, felsic igneous rocks show strong differentiated patterns between LREEs and HREEs coupled with strong negative anomalies of Eu. Considerations done on this subject also show that Eu/Eu^* can be utilized as an index of elemental conservation for determination of parental

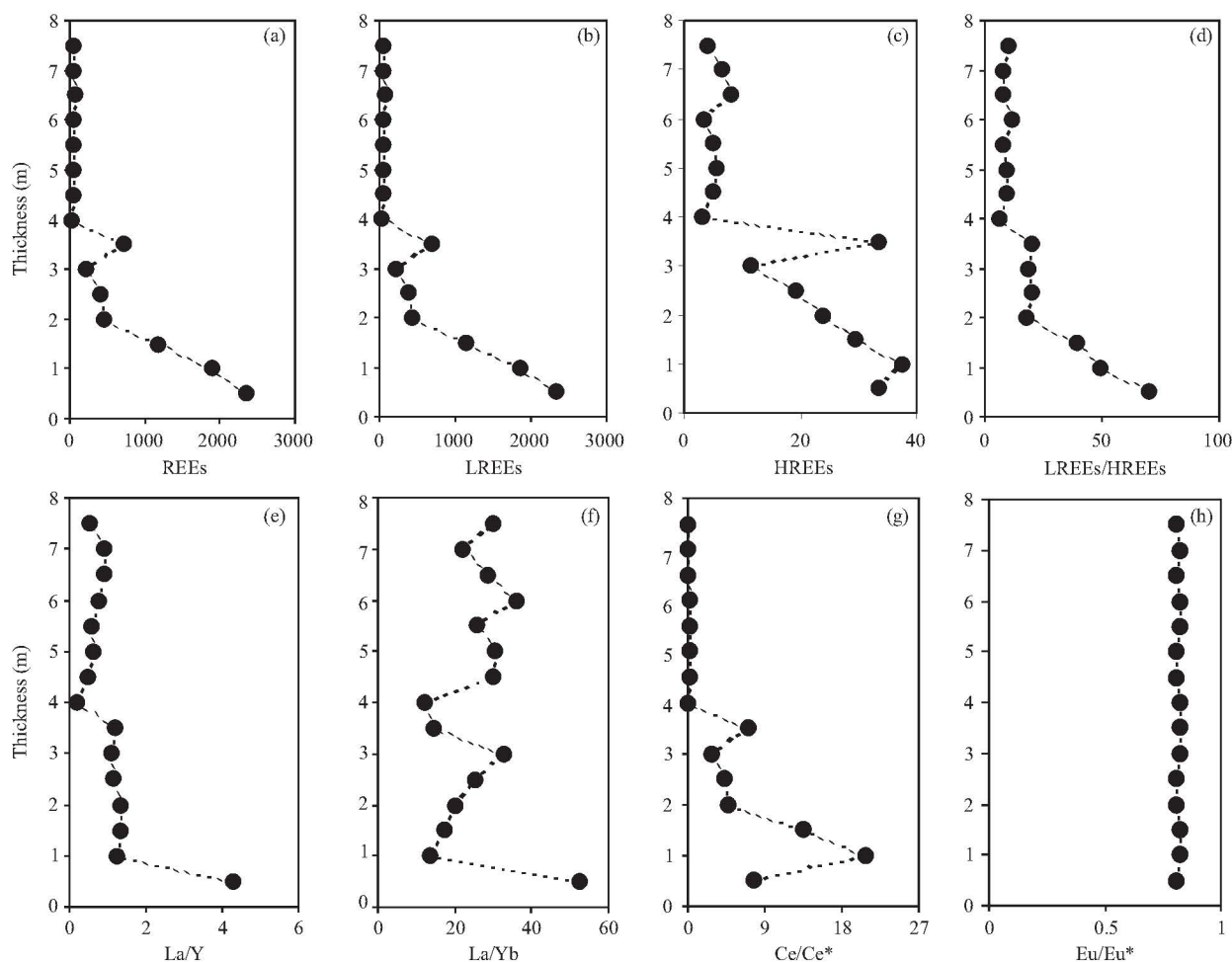


Fig. 3. Variation of values for (a) REEs, (b) LREEs, (c) HREEs, (d) LREEs/HREEs, (e) La/Y, (f) La/Yb, (g) Ce/Ce*, and (h) Eu/Eu* in the lateritic ores at studied profile.

affinity in weathered environments (Mongelli, 1997; Mameli et al., 2007). By taking this premise, the distribution aspects of REEs and Eu/Eu* index in the lateritic ores were used for determination of precursor of the deposit in this study. Distribution pattern of REEs normalized to chondrite (Taylor and McLennan, 1985) indicates relatively weak differentiation of LREEs (La–Gd) from HREEs (Tb–Lu) and occurrence of weak negative anomalies of Eu during lateritization (Fig. 4). These aspects suggest a basic igneous origin for the deposit. With regarding Eu anomalies (0.81–0.82) in the lateritic ores, Eu anomaly values in the basalt and carbonate bedrocks were calculated by using equation $Eu/Eu^* = Eu_N / (\sqrt{Sm_N} \times Gd_N)$. The calculated values show ranges 0.81–0.83 (with a mean of 0.82) and 0.41–0.47 (with a mean of 0.44) for the basalt and the carbonate bedrocks, respectively. By accepting Eu anomaly to be conservative during weathering processes and noting the similarity of its anomaly values in the lateritic ores to that of the basaltic rocks and more significantly the substantial disparity of Eu anomaly values between the carbonate

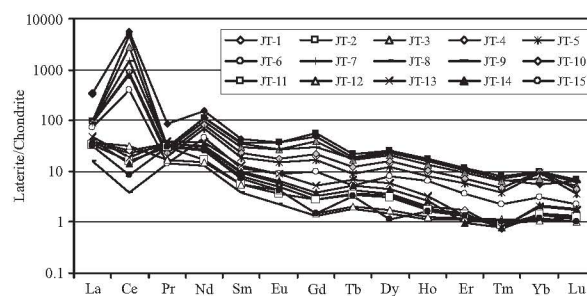


Fig. 4. Distribution pattern of REEs normalized to chondrite (Taylor and MacLennan, 1985) in the lateritic ores.

bedrocks and the lateritic ores, it can be conceived that Sheikh-Marut lateritic deposit is genetically related to alteration and weathering of basaltic rocks existing in the area.

4.2.4 Mass changes of REEs during lateritization

Mass change calculations can provide invaluable information on relative mobility and redistribution of elements during weathering processes. So far, various methods for calculations of mass change during alteration

and weathering processes were suggested by many workers including methods of volume factor (Gresens, 1967), isocon (Grant, 1986), immobile element (MacLean, 1990). In this study, however, method of immobile element (MacLean, 1990) was applied for mass change calculations in REEs. In this method, it is primarily necessary to select an immobile element (as monitor) showing the least variations during weathering processes, and then relative to it the mobility and enrichment or depletion of other elements are measured. Customarily, Al, Ti, Zr, Nb, Th, and Sc act as immobile elements during weathering processes (Gong et al., 2011). The variation trends of these elements in the profile illustrated that Sc have relatively the least variability during weathering processes. Thus, its abundance in the lateritic ores and basaltic rocks was taken as a basis for mass change calculations of REEs. The mass change calculations using immobile element method (MacLean, 1990) were implemented in three stages. First, the enrichment factor (EF) was calculated for each individual lateritic ore sample by using equation:

$$EF_{(\text{enrichment factor})} = Sc_{\text{basalt}} / Sc_{\text{laterite}}$$

Then reconstructed composition (RC) was computed by using the equation:

$$RC = EF \times \text{rare earth element in laterite}$$

Finally the degree of mass changes of REEs in each individual ore sample was determined by using the equation:

$$MC_{(\text{mass changes})} = RC - \text{precursor}$$

The obtained results from mass change calculations are presented graphically in Fig. 5a–n. The important conceivable conclusions from these diagrams are as follows:

(1) Two competing processes, namely leaching and fixation are the main regulating factors in concentration variation of REEs during lateritization.

(2) LREEs along with Tb and Dy were leached from the upper parts of the profile and precipitated in the lower parts.

(3) The highest concentrations of REEs occurred frequently adjacent to the contact of deposit with carbonate bedrocks.

(4) HREEs such as Ho, Er, Tm, Yb, and Lu were leached out of the system during lateritization.

5 Discussion

High concentration of Σ REEs of the ores was observed near the contact with the carbonate bedrocks (Fig. 3a). This may be due to the authigenic formation of REE-bearing minerals at the base of this deposit as well as the function of carbonate bedrocks as geochemical barrier and active buffer (Maksimovic and Panto, 1991). The increase of Σ REEs values from top toward bottom of the profile especially in quite regular and systematic fashion in the lower parts by approaching to the bedrocks (Fig. 3a) may indicate in-situ lateritization processes (Maksimovic and Panto, 1991). The most important anomalous levels in

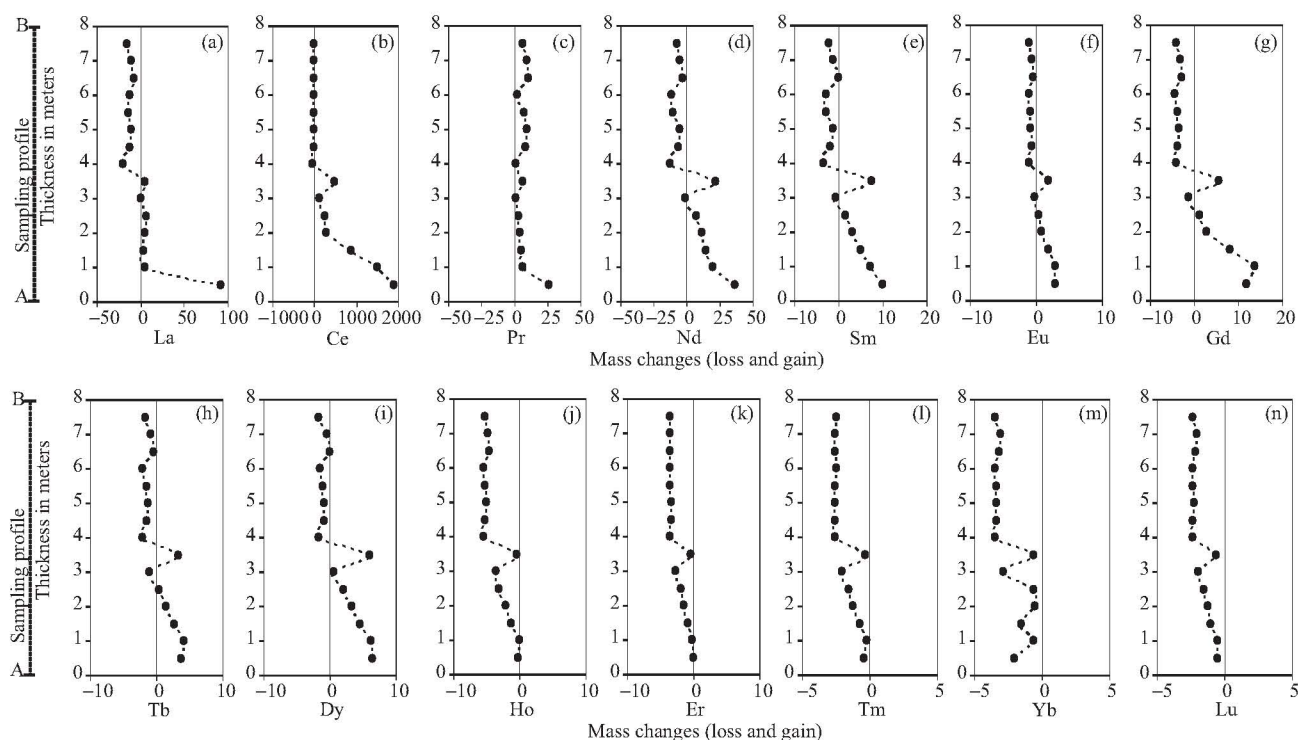


Fig. 5. Mass changes of REEs (by taking Sc as immobile monitor element) in the lateritic ores at studied profile.

variation of REEs in this deposit are the differentiation and enrichment of LREEs relative to HREEs with approaching to the carbonate bedrocks (Fig. 3d). What can be deduced from this differentiation and enrichment is that the pH of weathering solutions steadily increased while approaching to the carbonate bedrocks. This is because the stability of HREEs-complexes is relatively greater than that of LREEs in alkaline pHs (Ronov et al., 1967; Muchangos, 2006). It was demonstrated that values of $\text{La/Y} < 1$ and $\text{La/Y} > 1$ in residual ores are indicative of acidic and alkaline environments, respectively (Crinci and Jurkovic, 1990). Values of $\text{La/Y} < 1$ (from the upper parts of the profile) and $\text{La/Y} > 1$ (from the lower parts of the profile) may provide reasons to believe that acidic conditions (due to the dissolved CO_2) were prevailed in the meteoric percolating waters (Fernandez-Caliani and Cantano, 2010). These acidic solutions were probably neutralized by rising underground water table level causing the differentiation and enrichment of LREEs and HREEs in the lower parts of the profile.

By referring to the distribution pattern of REEs normalized to chondrite (Fig. 4), the discrepancy in degree of mobility of REEs may be regarded as one of the effective factors controlling their distribution during weathering processes. The low mobility of LREEs compared to HREEs caused the differentiation among REEs. Similarly differences in mobility between Ce and REEs led to the creation of Ce anomaly in the weathered products. Furthermore, moving of most REEs from the upper parts and precipitation of LREEs in the lower parts of the profile may be reasoned by the controlling role of pH variations in distribution of REEs in the ores (Fig. 4). By noting to the fact that the low and high pHs cause mobility and precipitation of REEs, respectively in the weathered environments (Pantino et al., 2003), it can be conceived that pH variation in ore-forming solutions was a basic and significant parameter in distribution of the REEs in this deposit. The important key point concerning mass changes of REEs during lateritization is the leaching of Ce from the upper parts and its precipitation in the lower parts of the profile (Fig. 3g). The existence of good and positive anomalies of Ce in the lower parts of the profile can be owing to the preferential precipitation of Ce in the form of cerianite (Braun et al., 1990). Moving of the Ce from the upper parts and its precipitation in the form of cerianite in the lower parts of the profile may be because of the effective role of Eh variation (due to the fluctuation of water table level) and pH increase of percolating waters during the evolution of the deposit (Braun et al., 1990). Considerations done elucidated that the sharp variations of Ce anomaly values across the studied profile (Fig. 3g) conform to the boundary between the red and brownish

red lateritic facies. It appears that the underground water table level rose up to this boundary. Therefore, it can be rational that the boundary of these two lateritic facies to be regarded as the paleo-level at which the downward percolating meteoric waters met and mixed with the underground water table.

By comparing the mode of mass changes of REEs (Fig. 5a–n) with Ce anomaly (Fig. 3g) in the profile, the effective role of organic matters in distribution of REEs in the ores can be deduced. Customarily, in severely weathered environment, the dissolved organic matters can cause the mobility of REEs (Oliva et al., 1999; Braun et al., 2005). By taking the variation trend of Ce anomalies into consideration, it can be envisaged that the complexation of dissolved organic matters with REEs brought about leaching of most REEs from the upper parts of the profile. These complexes with approaching to the carbonate bedrocks (due to the fluctuation of underground water table level and ensuing oxidation) broke down and lost their carrying capacity. As a result of this process the LREEs along with Tb and Dy were enriched in the lower parts of the profile. The prevalence of alkaline pH conditions in the lower parts of the profile, formation of stable HREEs-carbonate complexes due to buffering of weathering solutions by carbonate bedrocks can be the sole logical reason for leaching of HREEs such as Ho, Er, Tm, Yb, and Lu from the system (Cantrell and Byrne, 1987). It was established that REEs under neutral to alkaline conditions are fixed by processes such as scavenging and substitution in the weathered system (Muzaffer-Karadağ et al., 2009; Wang et al., 2010). Therefore, it is likely that scavengers and fixing minerals played a significant role in distribution of REEs in the lower parts of the profile. Many groups of minerals were proposed as hosts for REEs in weathered products including clay minerals, secondary phosphates, diaspore, Ti-oxides, and scavengers such as oxides and hydroxides of iron and manganese (Ma et al., 2007; Muzaffer-Karadağ et al., 2009; Wang et al., 2010). The existence of moderate to good positive correlations between Al and REEs (except Pr) ($r=0.53\text{--}0.94$) indicate that diaspore due to diadochic substitution played a crucial role in fixation of REEs in the deposit (Table 4). The weak negative and weak positive correlations between Fe and REEs ($r=-0.06$ to 0.57) and good and negative correlations between Si and REEs (except Pr) ($r=-0.50$ to -0.84) testify to feeble role of hematite and clay minerals in concentration of REEs, respectively (Table 4). The good and positive correlations between Mn and REEs ($r=0.52\text{--}0.90$) and also moderate to good positive correlations between phosphorous and REEs ($r=0.45\text{--}0.94$) (Table 4) illustrate that scavengers such as oxides and hydroxides of Mn

Table 4 Pearson correlation coefficient values among major elements and REEs in the lateritic ores at Sheikh-Marut

	Si	Al	Fe	Ca	Mg	Na	K	Ti	Mn	P
La	-0.50	0.53	0.40	-0.07	-0.15	-0.55	0.32	0.40	0.71	0.84
Ce	-0.63	0.75	0.42	-0.23	-0.20	-0.49	0.01	0.61	0.80	0.94
Pr	0.00	0.07	-0.06	-0.13	0.24	-0.12	0.10	-0.09	0.52	0.76
Nd	-0.76	0.85	0.50	0.03	-0.32	-0.54	0.02	0.70	0.90	0.82
Sm	-0.74	0.85	0.45	0.02	-0.28	-0.50	-0.07	0.70	0.90	0.83
Eu	-0.78	0.89	0.49	-0.06	-0.32	-0.50	-0.08	0.75	0.87	0.84
Gd	-0.77	0.89	0.49	-0.12	-0.33	-0.48	-0.10	0.75	0.85	0.84
Tb	-0.75	0.88	0.44	0.00	-0.29	-0.44	-0.17	0.73	0.88	0.79
Dy	-0.81	0.91	0.52	0.04	-0.36	-0.50	-0.09	0.78	0.88	0.77
Ho	-0.84	0.94	0.55	0.04	-0.40	-0.52	-0.07	0.81	0.87	0.75
Er	-0.84	0.92	0.56	-0.05	-0.40	-0.56	-0.06	0.80	0.85	0.77
Tm	-0.84	0.94	0.55	-0.03	-0.38	-0.57	-0.09	0.82	0.83	0.73
Yb	-0.84	0.89	0.57	0.17	-0.53	-0.51	-0.04	0.79	0.68	0.45
Lu	-0.82	0.91	0.54	0.03	-0.36	-0.51	-0.09	0.80	0.86	0.77

along with secondary phosphates were the important hosts for REEs in this deposit.

6 Conclusions

(1) Incremental trend of Σ REEs values from top to bottom of the profile indicate in-situ lateritization during the evolution of this deposit.

(2) Distribution pattern of REEs and index values of Eu/Eu* in the ores provide evidence concerning discrepancy in degree of mobility of REEs during lateritization and a mafic origin (basaltic rocks) for this deposit.

(3) Values obtained from mass change calculations of REEs (by taking Sc as immobile monitor element) implicate the dual role of carbonate bedrocks in distribution of REEs in the studied deposit. It appears that the carbonate bedrocks owing to buffering of percolating weathering solutions and hence destruction of REEs-organic complexes caused the deposition of LREEs, Tb, and Dy in the lower parts of the deposit. Formation of HREEs-carbonate complexes led to the leaching of Ho, Er, Tm, Yb, and Lu from the weathered system.

(4) The strong and positive anomalies of Ce in the lower parts of the profile may indicate the preferential deposition of Ce in the form of cerianite in the deposit. This may be reasoned by the change of chemistry (oxidation potential) of the ore-forming solutions and increase of pH in percolating waters.

(5) Interpretation of correlation coefficients among major oxides and REEs attest to the controlling role of scavengers such as oxides and hydroxides of manganese along with secondary phosphates, diaspore, and anatase in distribution of REEs in the studied deposit.

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