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Ree Chemistry of Arid Zone Calcrete Profiles-A Case Study From The Thar Desert, India

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Abstract: Calcrete is the widely prevalent duricrust associated with the weathering profiles of the Thar desert. The studies on REE behaviour within different weathering horizons of calcrete profiles, have revealed distinct pattern of enrichment and depletion. Fractionation of REE as evidenced through La/Lu, La/Sm, Nd/Dy ratios and removal index, are attributed to pedogenic processes such as breakdown of micas, pyroxenes, amphiboles, feldspars; removal of elements as soluble complexes; selective fixation of elements in neoformed clay minerals like montmorillonite, illite and chlorite. Sesquioxides rich Bir horizon shows enrichment of REE. REE depletion in Palaeo- Bt horizons could be due to their removal in solution as organic complexes.

Arid Zon Kaliş Profillerinde REE Kimyası, Thar Çölü (Hindistan)

Özet: Kaliş Thar çölünde ayrışma profillerinde yaygınca bulunan bir sert kabuk (duricrust) oluşumudur. Kaliş profillerinin farklı ayrışma düzeylerinde REE dağılımında belirgin zenginleşme ve fakirleşme belirlenmiştir. La/Lu, La/Sm ve Nd/Dy oranları ve "removal" indeks verilerinin gösterdiği gibi REE fraksiyonlaşması, toprak oluşum sırasında mika, piroksen, amfibol ve feldispat minerallerinin değişime uğramasına, çözülebilir bileşiklerden elementlerin uzaklaştırılmasına ve montmorillonit, illit ve klorit gibi yeni oluşan kil menarallerinide seçilmiş elementlerin biraraya gelmesine bağlanmıştır. Btr seviyesi REE zenginleşmesi gösterir. Paleo-Bt seviyesinde görülen REE fakirleşmesi organik bileşiklerin gözünerek uzaklaştırılmasına bağlı olarak gelişmiş olabilir.

Introduction

The REE's application in sediment provenance studies has been advocated because of their low solubility and fractionation under weathering conditions (Wildeman et al., 1973; Nance et al., 1977). However, subsequent researchers (Nesbitt, 1979; Hole et al., 1992; Ohr et al., 1994; Subrahmanyam and Singh, 1997) have clearly established fractionation, selective enrichment and mobilization of REEs within a weathering regime. The impact of weathering on REE distribution within a weathering profile depends upon both rock type and climatic conditions. REE fractionations in weathering profiles from warm-humid climatic regimes are well documented (op.cit.). However, similar observations from the weathering profiles of arid and semi-arid conditions still need to be properly understood. The present study on the REE chemistry of calcretic profiles developed under arid and semi-arid conditions is of great significance in understanding the microenvironmental conditions during calcretization.

Geo - Environmental Characteristics

The Thar desert is characterized by extreme diurnal and secular variations in temperature (mean maximum 42°C and minimum 27°C), low precipitation (between 250 & 300 mm), high potential evapo-transpiration (1500 - 2060 mm) and wind velocity. Climatically, the Thar desert on the E-W transect is characterized by semi-arid, arid and hyper-arid environments respectively.

The geomorphic features of the investigated area comprise fossil and active dunes, interdunal plains, saline depressions, rocky pediments and granitic/ rhyolitic / sandstone inselbergs. The geology of the area is represented by numerous litho-stratigraphic sequences ranging in age from the Precambrian to Tertiary periods. Varied lithologies including granites, rhyolites (Precambrian), sandstones, shales and limestones (Jurassic & Cretaceous), and sandstones, shales, limestones and evaporites (Tertiary), are enveloped by the dune sands of the Quaternary-Holocene periods (Pareek, 1981). These rock masses and unconsolidated sediments in conjunction with the climatic parameters underwent weathering and developed a variety of duricrusts.

Results and Disccusion

Field Characteristics

Within the study area, calcrete (the calcium carbonate duricrust) is the most conspicuous and widely distributed residual deposit. Prevalent forms of calcretes in the investigated area are powdery calcrete, nodular calcrete, coalesced nodular/honeycomb calcrete and hardpan calcrete. These calcretes are part of weathering profiles associated with stabilized dunes, interdunal plains and weathered pediments. An ideal calcrete profile exhibits development of different forms in the following sequence, from top to bottom:

Calcified soil

Powdery calcrete

Nodular calcrete - soft, diffusive

Nodular calcrete - hard, discrete

Honeycomb calcrete

Hardpan calcrete

Unaltered parent rock/sediments.

Mineralogy and Petrography

Petrographic and X-ray diffraction studies (Table 1) of calcretic profiles revealed that calcretes are predominantly comprised of calcite (5.4 - 70.5%), dolomite (1.2 - 42.2%) and quartz (19.7 - 54 %) with an increasing percentage of carbonates from powdery calcrete to hardpan type. In addition to these three major constituents; micas, pyroxenes, potash feldspars and amphiboles were also observed. The heavy minerals of the calcretized dune sands as determined by Raghavan et al.(1986) include garnet, zircon and tourmaline. The important neoformed clay minerals are comprised of chlorite, montmorillonite and illite.

Micromorphological studies of these calcrete profiles display different forms of pedogenic carbonates, in situ weathering of minerals, neoformations and clay illuviation features, indicating a clear pedogenic origin of calcretes (Ramakrishnan, 1997).

Ree Chemistry

In order to determine REE chemistry, calcrete samples and associated solum representing different horizons of weathering profile were collected from six representative profiles (Figure 1). Solutions of these samples were prepared by the standard HF-$HClO_4$ digestion technique. REE concentrations in the samples were estimated by ICP-MS (Walsh et al., 1981) and calibrated with the USGS standards Sco-1, SGR-1 and Sdo-1. The sample batches were regularly interspersed with standards and blanks. Estimated REE concentrations are normalized to upper crust (Rollinson, 1992) for graphical representation.

REE concentrations and fractionation-sensitive ratios (Balashaov et al., 1964) for all the sampled calcrete profiles were estimated (Table 2). It is worth noting from the REE abundance patterns that REE concentrations vary widely within different weathering horizons of calcrete profiles (Figure 2 A-F). Furthermore, it is apparent that the consistency of variation in LREE concentration is more pronounced than in HREE concentration.

The REE abundance pattern of the Dhanola profile (Figure 2A) shows marked depletion in REE concentration at Palaeo Bt horizon (weathering horizon comprising clay accumulation). The underlying horizon with illuvial accumulation of sesquioxides (Bir horizon) however, shows manifold increase in REE concentration.

The degree of variation in concentration at different horizons is further elucidated by variations in upper crust normalized ratios (La/Lu : 0.05 - 0.2; La/Sm : 0.9 - 1.2; and Nd/Dy :1.2 -1.4) . These ratios further point out that variation in the LREE/HREE ratio is more prominent than LREE/MREE, MREE / HREE ratios.

The estimated removal index ρ (where ρ = [Cp- Cm] / Cp helps in comparing the concentration of individual REE in the weathered solum [Cm] to the unaltered source [Cp]) also point to increase and decrease of REE concentration at different horizons with respect to the unaltered source (Ronov et al., 1967). The positive indices of ρLa, ρCe and ρTb in the palaeosol (Bt horizon) and negative indices of the corresponding elements in the underlying Bir horizon clearly point to REE depletion in the Bt horizon and enrichment in the Bir horizon. Similar REE depletion phenomenon in the palaeosol (palaeo Bt) horizon is also evidenced in the Bhaleri calcrete profile (Figure 2E).

In the Raneri calcrete profile, LREE fractionation is clearly evident from the REE abundance pattern (Figure 2 B) and the La/Lu (0.08 – 0.6) and La/Sm (0.8-1.05) ratios. The obtained fractionation sensitive ratios, removal index (Table 2) and abundance patterns of REEs at other locations such as Surpalia, Sardarsahar, Bhaleri and Belwa (Figure 2 c, d, e & f), clearly suggest that within these calcrete profiles the following are true:

Table 1. Mineralogy of calcrete profiles

Location	Horizon	Mineralogy (%)								
		Ch	Mont	Ill.	Q.	F	Cal.	Dol.	Bio	Goe.
Dhanola	Bt	15.3	11.8	10.9	21.4	5.26	23.6	6.1	----	-----
	Bir	18.2	11.2	9.6	30.4	9.9	3.04	13.8	-----	-----
	C	19.2	4.2	11.8	30.5	6.7	23.2	4.2	-----	-----
Sardarsahar	Bk	18.9	6.4	-----	22.9	2.7	29.0	14.4	4.5	1.6
	Cc	21.4	9.8	-----	39.0	14.0	5.4	4.0	6.7	-----
	C	15.5	5.8	-----	54.0	0.2	5.5	5.5	6.0	-----
Bhaleri	Bt	9.2	10.2	----	25.0	10.0	20.8	20.5	3.7	-----
	Bir	5.3	4.6	----	22.0	2.5	20.8	40.7	3.6	1.2
	K	5.2	5.2	----	19.7	1.8	20.5	42.2	3.6	1.5
	C	10.0	6.3	----	39.8	11.6	30.0	-----	4.2	-----
Belwa	Ac	-----	-----	-----	22.8	2.4	70.5	-----	4.3	-----
	AB	4.3	6.0	-----	51.3	14.8	14.6	4.6	2.9	-----
	Bc	8.8	3.3	-----	37.2	8.2	38.3	1.2	3.0	-----
	K	1.3	-----	-----	28.2	3.4	63.9	-----	3.3	-----

Ch . - Chlorite , Mont. - Montmorillonite, Ill. - Illite , Q – Quartz, F - Potash Feldspar, Cal. – Calcite, Dol - Dolomite, Bio . - Biotite, Goe. - Goethite.

A - Surface horizon rich in organic and mineral matters

B - More weathered horizon below A, enriched in clay /sesquioxides

AB - Junction between A & B horizons

K - Massive horizon formed due to heavy impregnation of carbonates

C - Horizon slightly more weathered than the fresh rock with limited accumulation of clay/sesquioxides.

Bt - B horizon with accumulation of clay

Bir - B horizon with accumulation of sesquioxides

Ac/Bc/Cc - A/B/C horizon with nodules/ concretions.

Bk–B horizon with accumulation of carbonate less than k horizon

1. REEs show significant variation in concentration at different weathering horizons. The well pedogenized Bt horizons are generally depleted in REE content. Horizons rich in lime concretions (Ac & Bc horizons) do not show any significant trend in REE migration, whereas the heavily carbonate-impregnated k horizon and the sesquioxide-rich Bir horizon exhibits enrichment in REE content.

2. Wider variation prevails in LREE concentration than in HREE concentration at different horizons, indicating a clear REE fractionation .

   Statistical analysis (Table 3) of REEs and sesquioxides (Fe, Mn) points to the existence of statistically significant, positive correlations among the LREEs (R = 0.99-0.96); and between the LREEs and sesquioxides (R = 0.64 – 0.60).

Table 2. REE chemistry of calcrete profiles

Sa.No	Loc.	Horiz	Dep.	La	Ce	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Lu	La/Lu*	La/ Sm*	Nd/Dy*	pLa	pCe	pTb	pLu
1	Dhanola	AB	100	3400	8400	920	3600	420	440	100	340	60	180	180	0.20	1.22	1.42	----	----	----	----
2		Bc	205	3200	7600	820	3200	460	460	100	340	60	180	220	0.16	1.05	1.27	+0.1	+0.1	0.0	-0.2
3		Bt	300	2200	5200	580	2400	340	300	60	260	60	140	180	0.13	0.94	1.24	+0.4	+0.4	+0.4	0.0
4		Bir	350	3600	9400	960	4000	540	760	120	380	80	180	680	0.05	1.00	1.41	-0.1	-0.1	-0.2	-2.8
5	Raneri	A	20	2000	3800	500	2000	320	300	80	280	60	160	260	0.08	0.94	0.96	----	----	----	----
6		Ac	50	2000	2600	520	1800	380	380	80	340	80	160	240	0.09	0.80	0.71	-0.1	-0.1	0.0	+0.8
7		Ac	75	3000	7400	820	3200	500	540	120	380	80	220	360	0.09	0.91	1.12	0.0	0.0	-0.2	-0.3
8		Bc	100	3200	7800	820	3200	460	520	100	380	60	200	60	0.57	1.05	1.13	+0.3	+0.6	+0.2	+0.1
9		Bk	150	3000	7200	740	3200	500	540	100	400	80	200	280	0.11	1.00	1.07	+0.3	+0.5	+0.2	+0.1
10	Surpalia	Ac	110	3000	6800	740	3000	500	520	120	380	80	180	240	0.13	1.00	1.06	----	----	----	----
11		Bc	210	2000	3400	480	1800	320	320	80	280	60	140	200	0.11	0.94	0.86	+0.3	+0.5	+0.3	+0.2
12		C	300	2400	4800	620	2400	360	380	80	280	60	140	260	0.09	1.00	1.15	+0.2	+0.3	+0.3	-0.1
13	Sardarsar	Bk	100	2000	4800	480	2000	380	420	100	300	60	160	220	0.10	0.80	0.89	-----	-----	-----	-----
14		Bk	175	2000	4200	480	1800	340	340	80	240	60	140	260	0.08	0.85	1.02	0.0	+0.1	+0.2	-0.2
15		Cc	220	2600	6400	660	2800	340	424	80	300	60	160	260	0.10	1.12	1.25	-0.3	-0.3	+0.2	-0.2
16		C	300	3000	8000	760	3000	420	480	100	320	60	180	240	0.13	1.08	1.26	-0.5	-0.7	0.0	-0.1
17	Bhaleri	A	120	2000	4200	460	1800	380	360	80	280	60	140	240	0.09	0.80	0.86	-----	-----	-----	-----
18		Bt	160	1800	3800	440	1600	280	300	60	240	40	120	220	0.09	0.97	0.90	+0.1	+0.1	+0.1	+0.
19		Bir	220	3400	8400	860	3200	460	400	100	380	80	200	240	0.16	1.12	1.13	-0.7	-1.0	-0.3	0.0
20		K	350	3400	8400	860	3400	480	440	100	380	80	180	300	0.13	1.06	1.20	-0.7	-1.0	-0.3	-0.3
21	Belwa	Ac	120	1200	2600	260	1200	240	160	60	240	60	160	300	0.04	0.75	0.67	----	----	----	----
22		Bc	300	4000	9800	1000	4200	560	480	100	400	80	240	360	1.18	1.08	1.42	-2.3	-2.8	-0.7	-0.2
23		K	400	3200	6800	740	2800	440	340	100	360	80	220	320	0.12	1.09	1.05	-1.7	-1.6	-0.7	-0.1
24		C	500	1600	3800	380	1600	300	240	80	240	60	160	280	0.06	0.79	0.90	-0.3	-0.5	-0.3	+0.7

REE concentrations are in ppb.

* Values normalized to Upper Crust

	Fe	Mn	La	Ce	Nd	Sm	Er	Lu
Fe	1.00							
Mn	0.48	1.00						
La	0.64	0.43	1.00					
Ce	0.60	0.44	0.99	1.00				
Nd	0.56	0.36	0.99	0.99	1.00			
Sm	0.60	0.28	0.97	0.96	0.97	1.00		
Er	0.19	0.35	0.82	0.81	0.83	0.80	1.00	
Lu	-0.23	-0.23	0.42	0.46	0.54	0.50	0.78	1.00

Table 3. Correlation matrix of sesquioxides and REEs

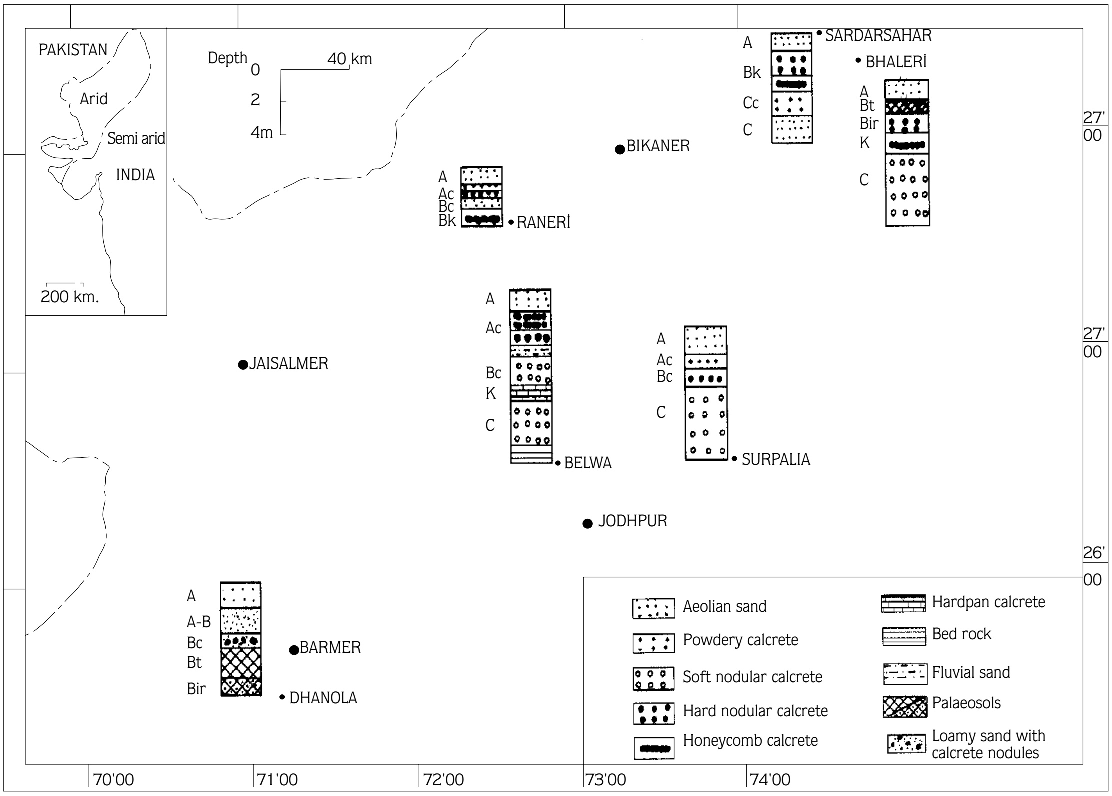

Figure 1. Location map of the study area with calcrete profiles investigated.

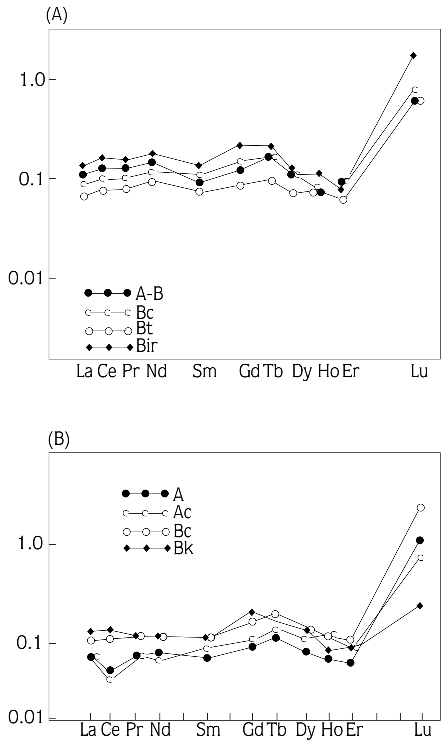

Figure 2ab. (A-F) Upper crust normalized REE abundance patterns
A- Dhanola profile; B- Raneri profile.

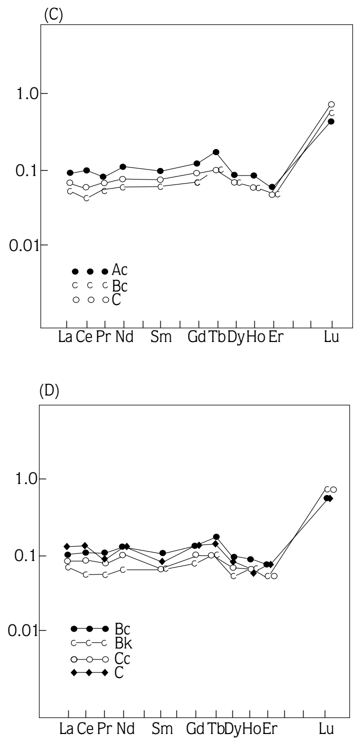

Figure 2cd. (A-F) Upper crust normalized REE abundance patterns
C- Surpalia profile; D- Sardarsahar profile.

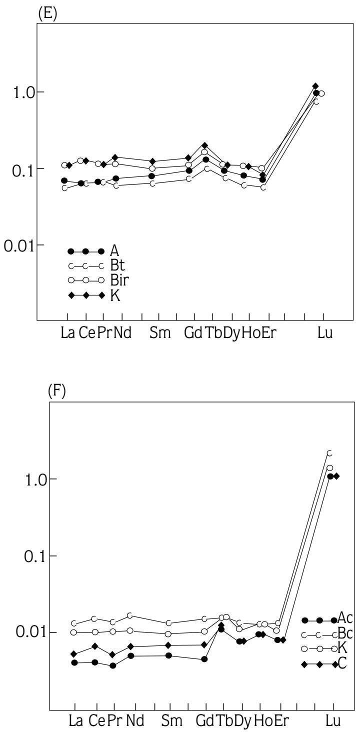

Figure 2ef. (A-F) Upper crust normalized REE abundance patterns E- Bhaleri profile; F- Belwa profile.

Multivariate regression analysis of the REEs among different profiles indicates that their mobilization behaviour varies from profile to profile. However, within an individual profile their behaviour is significantly related (F = 0.003-0.004).

Discussion

REE mobilization is generally facilitated in tropical weathering under warm-humid conditions by such processes as kaolinization, clay illuviation and lateritisation (Nesbit, 1979; Subrahmanyam and Singh, 1997). On the other hand, weathering profiles developed under semiarid-arid conditions are believed to be consistent in their REE abundance. The authors' observations, however, categorically point to REE fractionation and mobilization within the calcrete profiles developed under arid-semiarid conditions .

The REE behavioural pattern of calcrete profiles in question, supported by mineralogical and micromorphological studies (Ramakrishnan, 1997; Ramakrishnan and Tiwari, 1997), has led to the identification of three major factors governing REE fractionation and mobilization.

1. The pivotal role of pedogenic processes (weathering, neoformations, illuviation, displacive/replacive action of calcite, etc.) in effective liberation of REE from the parental material.
2. Chemical weathering under near neutral or alkaline microenvironment, which is responsible for the formation of soluble bicarbonate and organic REE complexes (Goldstein and Jacobson, 1988; Wood, 1990).
3. The role of neoformed minerals, such as montmorillonite, illite, chlorite and goethite and altered relicts of original minerals in selective retention and liberation of REEs under changing pH and Eh conditions (McKenzie, 1963; Bolt et al., 1967; Nesbit, 1979; Ohr et al., 1994).

In the calcrete profiles investigated, the degree of weathering in hornblende, biotite and potash feldspars range from simple bleaching to complete alteration to clay minerals such as montmorillonite, illite and chlorite. The liberation of Fe, Mn hydroxides during these alteration processes, their mobility within the profile and their accumulation (Bir horizons) are also well established (Ramakrishnan , 1997).

Furthermore, the mechanism of clay illuviation (responsible for the formation of Bir and Bt horizons), widely prevalent in many of these weathering profiles, facilitates mobilization and selective fixation of REEs (Haskin et al., 1968; Varshal et al., 1975; Subrahmanyam and Singh, 1997) under different microenvironments (Bolt et al., 1967) in different horizons.

REE depletion in the Bt -horizons of Dhanola and Bhaleri may be attributable to their removal under acidic to near neutral conditions. The REEs removed from the above horizons are trapped and fixed in the neoformed minerals under slightly alkaline conditions in the underlying horizons, thereby causing REE enrichment. Seasonal wetting along with mostly prevalent dry conditions in the study area ideally facilitate the operation of these processes. Statistical observations also support the fractionation of REE, and the affinity for sesquioxides.

Therefore, it is apparent from the foregoing discussions that the fractionation and mobilization of REEs take place during pedogenesis and calcretization. Fractionation, changes in the REE concentration within the calcrete profiles can be accounted mainly to different pedogenic processes such as mineral weathering,

neoformation of clays, clay illuviation, generation of Fe-Mn hydroxides and their movement within the profile.

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