

RARE EARTH ELEMENTS BEHAVIOR IN PERUÍBE BLACK MUD

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ABSTRACT

Rare earth elements in sediments have been used as powerful tools for environmental studies because of their behavior during geochemical processes and are also widely accepted as reliable provenance tracers because they are largely water-immobile and thus behave conservatively during sedimentary processes. The Peruíbe Black Mud (PBM) is a sedimentary deposit originated from the interactions of marine sediments and organic matter in an estuarine environment that originates a peloid currently used for medicinal purposes. The objective of this study was to examine rare earth elements pattern distribution in the Peruíbe black mud sedimentary deposit as a proxy for its geochemical development. Elemental ratios such as LaN/YbN, Th/U and La/Th were determined and a normalization of the mean rare earth elements concentrations in the samples related to NASC indicates that the light (La to Eu) rare earth elements present values close to the unity while the heavy (Tb to Lu) rare earth elements are depleted related to NASC. It can be observed that the light rare earth elements present enrichment values slightly enriched over the unity while the heavy rare earth elements present values generally below the unity reflecting the enrichment of the light rare earth elements over the heavy rare earth. Rare earth elements concentrations determined in Peruíbe black mud samples showed a distribution similar to that found in the NASC for the light rare earth elements and depleted for the heavy rare earth elements.

1. INTRODUCTION

Rare earth elements (REEs) in sediments have been used as powerful tools for environmental studies because of their behavior during geochemical processes [1-2]. REEs are also widely accepted as reliable provenance tracers because they are largely water-immobile and thus behave conservatively during sedimentary processes [3-4]. The potential of REE in contributing to such studies are related to their chemical properties (4f electronic configurations) being the trivalent state the cause of a coherent group behavior.

Different from the others rare earth elements, Ce and Eu can change their oxidation states into tetra and di-valence, respectively, according to redox conditions, which cause their unique and anomalous behavior compared with other REE. The REE abundance patterns may provide fingerprints in geochemical processes such as sediment provenance, contribution of detrital materials, authigenic components and redox conditions during deposition events [5-6].

The Peruíbe Black Mud (PBM) is a sedimentary deposit originated from the interactions of marine sediments and organic matter in an estuarine environment that originates a peloid currently used for medicinal purposes. The mud treatment is done in a therapeutic clinic called "Lamário" and this practice is nowadays sponsored by the Public Health Brazilian System (SUS – Sistema Único de Saúde). In the "Lamário", the mud directly collected from

the mud deposit, from now on called “*in natura* mud” is sieved, in a 2 mm aperture sieve, in order to separate any courser material, such as stones, leaves and pieces of branches. After that, the *in natura* mud remains in contact with sea water for long periods and this process is called maturation. The obtained product is called matured mud. The sea water used in the maturation is taken 2 km far from the coast. The maturation process lasts up to six months. During this period, the sea water is periodically changed twice a month. No agitation is employed.

The mud deposit location is shown in Figure 1. Mineralogical composition of this mud is predominantly quartz with small amounts of ilite, gypsum, kaolinite, feldspar and halite. The particle size distribution shows a range of 19 to 66% of silt plus clay and in average, 55% of sand. Physical chemically, the PBM presents mean pH of 6.8 and CEC varying from 26 to 36 meq/100g. Considering the chemical composition it is enriched in the elements As, Br, Cr, Sb, Se and Zn and depleted in the elements Ca, Rb and Ta when compared to the Upper Continental Crust (UCC) [7].



Figure 1: Location of Peruíbe City in Southeast Brazil.

The objective of this study was to examine REE pattern distribution in the PBM sedimentary deposit as a proxy for its geochemical development. Elemental ratios such as LaN/YbN, Th/U and La/Th were also determined.

2. METHODOLOGY

The PBM samples were analyzed by Instrumental Neutron Activation Analysis. Samples, after being crushed and sieved to a grain size smaller than 150 mesh, were irradiated together with a convenient reference material in a neutron flux of $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for 8 hours in the IEA-R1 reactor at IPEN. Counting for the determination of the REE, as well as, U and Th concentrations was made one and two weeks after irradiation depending on the formed radionuclide half-life. The induced activities were measured by using a Hiperpure Ge detector [8].

3. RESULTS AND DISCUSSION

The results of the REE, U and Th concentrations in the PBM samples as well as the NASC (North American Shale Composite) values are shown in Table 1. It can be observed that no difference exist between the *in natura* and matured forms indicating that the maturation process do not affect the rare earth composition in this samples.

Normalization of the mean REE concentrations in the samples related to NASC, also shown in Table 1 and in Figure 2, indicates that the light (La to Eu) rare earth elements (LREE) present values close to the unity while the heavy (Tb to Lu) rare earth elements (HREE) are depleted related to NASC. This pattern is expected in marine and estuarine sediments. Although acting as a group with high chemistry similarity, REE can be fractionated in solution presumably due to its gradual decrease in the ionic radius across the La–Lu serie [9]. LREE are preferentially removed from the solution and adsorbed in the surface of particles, such as Mn- and Fe-oxides and clay minerals or precipitates as REE phosphates [10], while the HREE typically form dissolved complexes which remain in solution [11].

Table 1: Rare earth and selected elements concentration, in $\mu\text{g g}^{-1}$, in PBM samples

	La	Ce	Sm	Nd	Eu	Tb	Yb	Lu	Th	U	Sc
IN1	31.11	62.84	4.93	22.03	1.15	0.60	1.48	0.27	8.4	2.4	11.77
IN2	19.83	39.40	3.13	16.73	0.75	0.30	0.99	0.16	5.1	1.6	7.38
IN3	37.37	76.04	5.92	30.63	1.38	0.56	1.72	0.29	9.7	3.4	13.45
IN4	26.96	53.30	4.31	30.98	0.96	0.63	1.63	0.26	8.4	2.5	8.90
IN5	24.59	49.85	3.92	23.31	0.90	0.42	1.22	0.22	7.6	2.8	8.53
IN6	42.19	89.11	6.67	41.08	1.56	0.61	2.10	0.33	12.6	5.2	16.28
IN7	38.38	78.35	6.02	36.99	1.23	0.66	2.00	0.31	12.1	4.4	12.63
IN8	42.44	83.56	6.12	40.38	1.28	0.62	1.87	0.35	12.8	5.9	13.34
IN9	26.78	52.68	4.13	24.48	0.82	0.47	1.64	0.25	8.9	5.0	9.23
Mean	32.18	65.01	5.02	29.62	1.11	0.54	1.63	0.27	9.51	3.68	11.28
SD	8.20	17.34	1.22	8.62	0.27	0.12	0.36	0.06	2.57	1.49	2.93
REE/NASC	1.03	0.97	0.90	1.08	0.94	0.64	0.53	0.59			
MAT1	24.96	48.72	3.82	23.66	0.89	0.48	1.28	0.22	7.3	2.3	8.44
MAT2	22.91	52.22	3.58	22.23	0.89	0.43	1.34	0.21	7.5	2.4	8.88
MAT3	30.18	55.53	5.01	28.43	1.14	0.47	1.28	0.23	7.5	3.4	10.55
MAT4	35.64	76.03	5.52	34.31	1.15	0.59	1.80	0.28	10.1	4.0	13.40
MAT5	39.75	82.18	6.15	35.12	1.36	0.70	1.71	0.31	11.2	4.5	14.01
MAT6	32.15	67.30	4.98	30.15	1.14	0.51	1.65	0.24	9.2	4.0	11.69
MAT7	35.11	68.43	5.74	50.62	1.28	0.67	1.38	0.26	10.4	3.2	11.29
MAT8	34.19	67.47	5.64	29.78	1.36	0.26	2.06	0.34	9.7	4.8	11.74
MAT9	35.53	71.41	5.90	45.44	1.49	0.75	2.11	0.32	10.0	3.5	12.57
MAT10	38.16	74.53	6.18	39.19	1.51	0.40	1.78	0.32	10.9	3.5	13.09
Mean	32.86	66.38	5.25	33.89	1.22	0.52	1.64	0.27	9.39	3.54	11.57
SD	5.44	10.91	0.92	9.09	0.22	0.15	0.31	0.05	1.46	0.80	1.85
REE/NASC	1.06	1.00	0.94	1.24	1.03	0.62	0.54	0.60			
NASC	31.10	66.70	5.59	27.40	1.18	0.85	3.06	0.46	12.30	2.66	14.90

The LREE enrichment is also highlighted by the (La/Yb)_n ratio, showed in Table 2, where the subscribe n means normalized for NASC with values varying from 1.6 to 2.3. In sea water the Sm/Yb ratio is typically 0.2, the preferential incorporation of the LREE to the PBM sediment is evidenced by the fact that this ratios in the samples varies from 1.38 to 2.15 (Table 2). No fractionation is observed for among the LREE as indicated by the (La/Sm)_n ratio (Table 2).

The enrichment factor (EF) is a widely tool applied as an index to reflect environmental contamination of sediment mainly due to anthropogenic contributions. It was here employed to evaluate possible input of REE to PBM samples [12-13] and calculated as: $EF = (REE/Sc)_{sample} / (REE/Sc)_{NASC}$. By definition, the enrichment factor close to unity (EF = 1) indicates, that the observed concentration of the element considered is due to natural variations of the environment and it originate from natural sources [14].

According to Birch [15] the contamination degree can be divided into different categories based on EF values. EF < 1 demonstrates “no enrichment”, EF < 3 is “minor enrichment”, EF = 3-5 is “moderate enrichment”, EF = 5-10 is “moderately severe enrichment”, EF = 10-25 is “severe enrichment”, EF = 25-50 is “very severe enrichment” and EF > 50 is “extremely severe enrichment”.

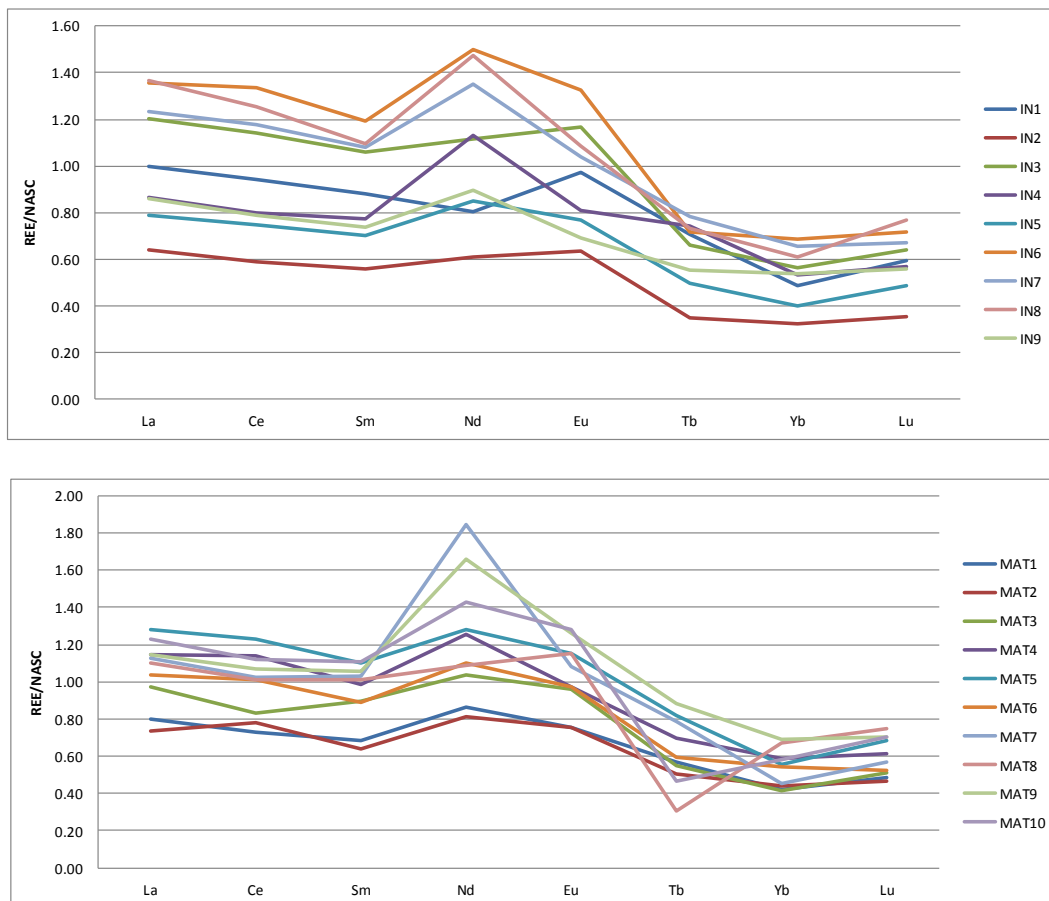


Figure 2: REE distribution pattern, normalized for NASC, in the *in natura* (A) and matured (B) samples of PBM.

The EF results for the *in natura* and matured PBM samples are shown in Table 3. It can be observed that the LREE present EF values slightly enriched over the unity while the HREE present values generally below the unity reflecting the enrichment of the LREE over the HREE. Nevertheless, the EF obtained classifies the PBM mud samples as of natural origin without anthropogenic inputs.

The discrimination plot of $(La/Yb)_n$ vs. $(Sm/Nd)_n$ is commonly used to distinguish different sources to REE concentrations in sediments. As shown in Figure 3, the homogeneous distribution presented in the samples suggests an unique source for the REE for the PBM. The good correlation between REE and Th, Sc and U also suggest a common source for these elements (Figures 4a to 4c). On the other hand, the lack of correlation with Ti (Figure 4d), a common element found in heavy minerals, indicated that the REE in the PBM samples are not bounded to these minerals.

Table 2: Cerium anomaly (Ce*), Σ REE and elemental ratios observed in PBM samples

	Σ REE	Ce*	La_n/Yb_n	Sm_n/Nd_n	La_n/Sm_n	Sm_n/Yb_n	U/Th	La/Th	Yb/Th
IN1	124.41	0.48	2.06	1.10	1.13	1.82	0.29	3.72	0.18
IN2	81.28	0.42	1.98	0.92	1.14	1.74	0.31	3.88	0.19
IN3	153.92	0.43	2.14	0.95	1.13	1.88	0.35	3.84	0.18
IN4	119.02	0.33	1.63	0.68	1.12	1.45	0.30	3.23	0.19
IN5	104.44	0.39	1.98	0.83	1.13	1.76	0.36	3.22	0.16
IN6	183.64	0.40	1.98	0.80	1.14	1.74	0.41	3.35	0.17
IN7	163.94	0.39	1.89	0.80	1.15	1.65	0.36	3.18	0.17
IN8	176.62	0.38	2.23	0.74	1.25	1.79	0.46	3.31	0.15
IN9	111.26	0.39	1.61	0.83	1.17	1.38	0.56	3.01	0.18
MAT1	104.04	0.38	1.91	0.79	1.17	1.63	0.32	3.42	0.18
MAT2	103.81	0.43	1.68	0.79	1.15	1.46	0.31	3.06	0.18
MAT3	122.25	0.36	2.32	0.86	1.08	2.15	0.45	4.02	0.17
MAT4	155.32	0.41	1.94	0.79	1.16	1.68	0.39	3.52	0.18
MAT5	167.28	0.42	2.29	0.86	1.16	1.97	0.40	3.54	0.15
MAT6	138.14	0.41	1.91	0.81	1.16	1.65	0.43	3.48	0.18
MAT7	163.49	0.27	2.50	0.56	1.10	2.27	0.31	3.39	0.13
MAT8	141.10	0.40	1.63	0.93	1.09	1.50	0.49	3.52	0.21
MAT9	162.96	0.31	1.66	0.64	1.08	1.53	0.35	3.56	0.21
MAT10	162.07	0.35	2.11	0.77	1.11	1.90	0.32	3.50	0.16

Table 3: Enrichment Factor (EF) obtained for the PBM samples

	La	Ce	Sm	Nd	Eu	Tb	Yb	Lu
IN1	1.27	1.19	1.12	1.02	1.23	0.89	0.61	0.75
IN2	1.29	1.19	1.13	1.23	1.28	0.70	0.65	0.71
IN3	1.33	1.26	1.17	1.24	1.29	0.73	0.62	0.71
IN4	1.45	1.34	1.29	1.89	1.35	1.24	0.89	0.95
IN5	1.38	1.31	1.23	1.49	1.34	0.86	0.70	0.85
IN6	1.24	1.22	1.09	1.37	1.21	0.66	0.63	0.65
IN7	1.46	1.39	1.27	1.59	1.23	0.92	0.77	0.79
IN8	1.52	1.40	1.22	1.65	1.21	0.82	0.68	0.86
IN9	1.39	1.27	1.19	1.44	1.12	0.89	0.87	0.90
MAT1	1.42	1.29	1.21	1.52	1.33	1.00	0.74	0.85
MAT2	1.24	1.31	1.07	1.36	1.26	0.84	0.73	0.78
MAT3	1.37	1.18	1.26	1.47	1.36	0.78	0.59	0.72
MAT4	1.27	1.27	1.10	1.39	1.08	0.78	0.66	0.68
MAT5	1.36	1.31	1.17	1.36	1.23	0.87	0.59	0.72
MAT6	1.32	1.29	1.14	1.40	1.24	0.76	0.69	0.67
MAT7	1.49	1.35	1.36	2.44	1.43	1.04	0.60	0.75
MAT8	1.39	1.28	1.28	1.38	1.46	0.39	0.85	0.95
MAT9	1.35	1.27	1.25	1.97	1.49	1.05	0.82	0.84
MAT10	1.40	1.27	1.26	1.63	1.45	0.53	0.66	0.80

In aquatic system Th is relatively immobile [16-17] and is present mostly in the detritus fraction [18]. Similarly, Sc, which is also another lithophile element associated with Th and U, is generally considered of terrigenous origin. The close association (Figure 4a to 4c) of the REE with Th, Sc and U in the PBM samples suggests the same provenance, also corroborated by the constancy of the La/Th ratio.

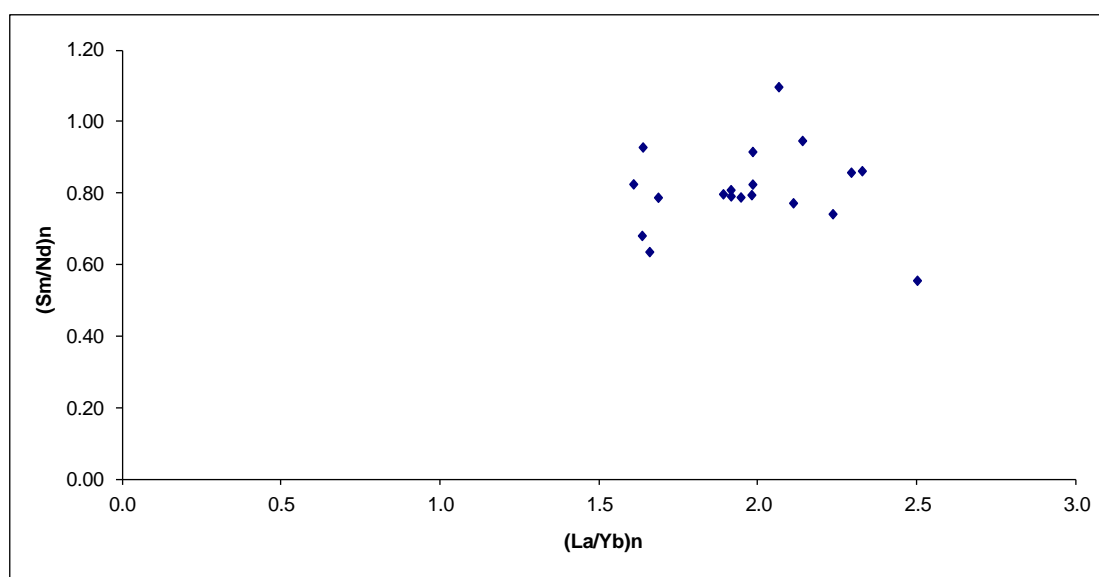


Figure 3: Discrimination plot of (La/Yb)_n vs. (Sm/Nd)_n of the PBM.

The U/Th ratio can be used to infer redox conditions during deposition of the sediment or to reflect the redox conditions of the source material. Generally, low U/Th ratios (<0.75) indicate well-oxygenated conditions, whilst high values (>1.25) indicate anoxic conditions, and those between 0.75 and 1.25 indicate dysoxic conditions [19]. The U/Th ratio of the analyzed samples, showed in Table 2, varies from 0.29 to 0.56 suggesting an oxic environment for the PBM source material containing REE in agreement with the terrigenous source suggested above.

The Ce-anomaly ($Ce^* = 3Ce_n / (2La_n + Nd_n)$) represents its enrichment or depletion compared to its neighboring elements [20]. A depletion of Ce relative to its neighbors give rise to a negative Ce^* and may result from the presence of calcareous and siliceous organisms. A positive Ce-anomaly results where Ce is enriched relative to its neighbors and might resulted from the presence of Fe–Mn oxyhydroxides [21].

Sediments of marine origin therefore tend to present positive Ce anomaly due to the scavenging of the Ce^{4+} from the solution and its incorporation into de sediment [22], in oxidic water, such as the costal water where the PBM deposit where formed. However, various factors, like detrital input, diagenetic alteration and REE exchange between pore water and sediment, may obscure the original Ce anomaly [23].

The observed negative Ce^* (Table 2) of PBM can be, therefore, a result of facts such as terrigenous contribution and the presence of s siliceous organisms organism, as observed by Torrecilha [7].

4. CONCLUSIONS

Rare earth elements concentrations determined in PBM samples showed a distribution similar to that found in the NASC for the Light REE and depleted for the Heavy REE. This pattern can be related to the interaction of the PBM sediment with sea water. Nevertheless, the elemental ratio study showed that the provenance of the RRE in these samples is most probably due to terrigenous input.

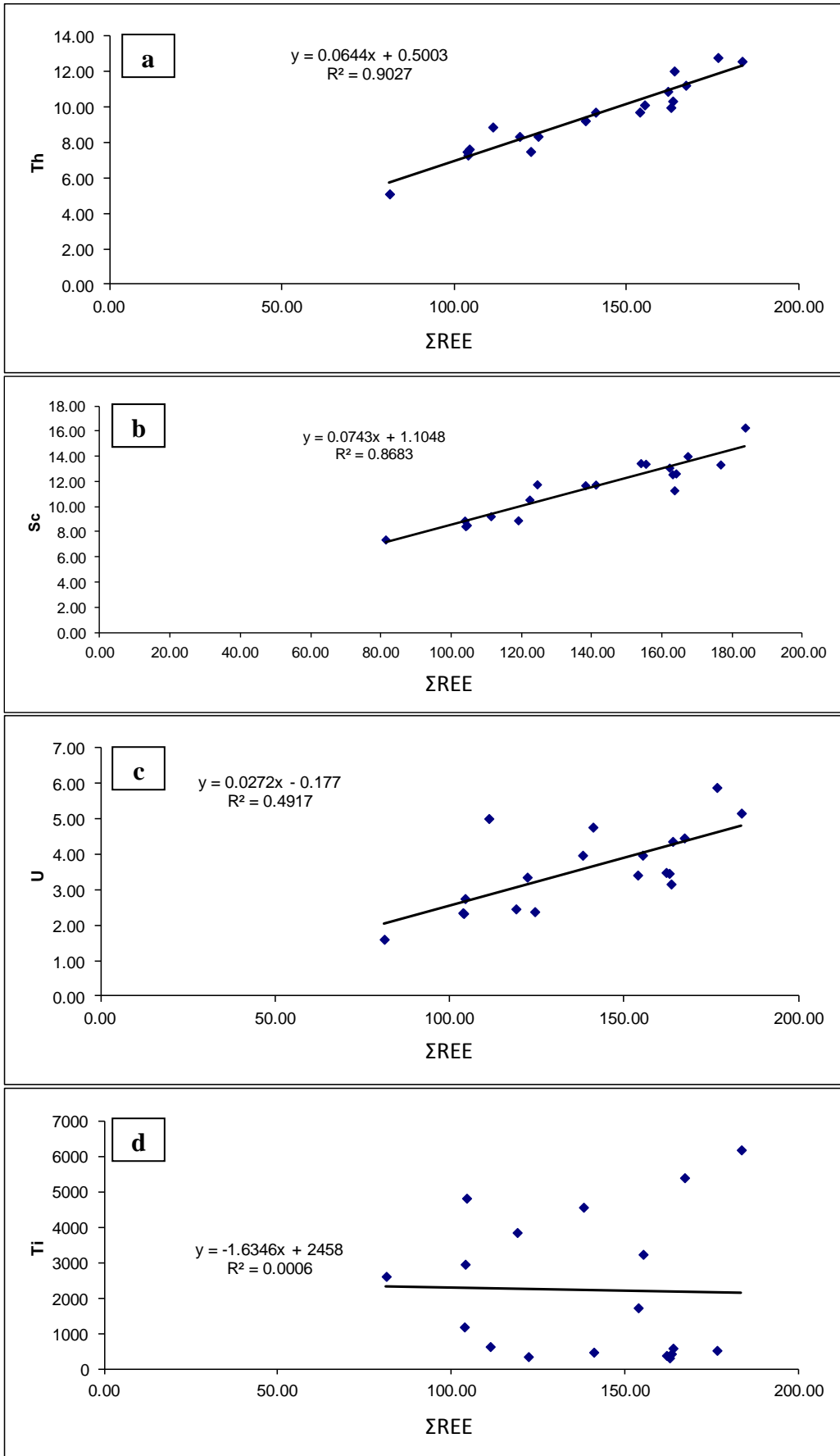


Figure 4: Correlation between ΣREE and (a) Th, (b) Sc, (c) U and (d) Ti.

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