Sources of rare earths and prospects for a viable REE deposit in river sediments of Kerala, southwest India

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Studies on rare earth elements (REEs) of river sediments from Kerala, India indicate that the average total REE (ΣREE) of clay and silt-sized fractions is much higher than in Post-Archaean average Australian Shale (PAAS). Peak high ΣREE for the clay fraction is found in the rivers of central Kerala and, for the silt fraction, it is in south and central Kerala. ΣREE shows a moderate to strong correlation with Mn and P and, no correlation with Al, Fe and Ti in both size fractions. ΣREE also shows no correlation with heavy metals in the clay fraction but a strong correlation in silt fraction. PAAS-normalized REE shows MREE-enrichment in almost all the samples. Further, LREE-enriched and HREE-depleted REE patterns are characteristic of sediments from south and central Kerala, and HREE-enriched or flat REE patterns are characteristic of sediments from north Kerala. Weak positive or weak negative Ce anomalies are characteristic of the sediments. The Eu anomaly is negative in a few silt fractions from south Kerala and positive in all other sediments. Sm/Nd ratios are high in the clay fraction and decrease with increasing ΣREE for the sediments of central Kerala. REE enrichment and REE patterns are related to the felsic component and heavy mineral content in the sediments of south Kerala, adsorbed REE associated with the weathering products of laterites in the sediments of central Kerala, and the dominance of mafic component in the sediments of north Kerala. The river sediments of central Kerala may serve as a viable REE deposit because of their high REE content, inexpensive mining, easy recovery and extraction of REE. Only 21 out of 41 rivers of Kerala were analysed in this study. Detailed exploration in other rivers may expand and confirm the potential REE deposits and their economic viability. This REE deposit is different from the placer sand deposits on the beaches of south Kerala.

Keywords: Clay and silt fractions, Kerala, laterite, rare earth elements, river sediments.

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RARE EARTH ELEMENTS (REEs) are a coherent group of elements widely used as tracers to understand better the geological evolution of the continental crust, provenance, palaeoclimate and palaeoceanography, geochemical and sedimentary processes associated with weathering, erosion, transport and deposition of sediments in the riverine, estuarine and marine systems, and diagenesis[1–14]. Chemical weathering of rocks is an important process, wherein mobile REEs are removed, and immobile REEs are enriched with the weathering products[15]. REEs thus are not only fractionated but also concentrated into REE deposits during lateritization of bedrocks[16–18]. Cocker[19] reported higher REE content in weathering profiles and laterites than in parent rocks. REE content was four times higher in the laterites than in granites from the Riau Islands, Indonesia[20]. Moreover, sedimentary REE deposits related to the chemical weathering of rocks, known as Ion-Adsorption-type Deposits (IADs), have been reported[21–25] and mined in South China[22,23].

The Kerala region is located in the southwestern part of peninsular India, and its landscape is covered by thick laterites. Bauxites have also been reported (Figure 1). At least 41 west-flowing, rainfed, minor and medium rivers drain the landscape of Kerala, bringing sediments from bedrock and laterites[26]. The river sediments are expected to contain weathering products of rocks and laterites, further modified by erosion and sorting processes which occurred during transport from the source to the sink site. The purpose of this study is to determine: (a) the REE sources in the clay and silt-sized fractions of sediments in the rivers of Kerala and the factors controlling their distribution and (b) indicate a viable REE deposit in the river sediments. This REE deposit is similar to IAD, being reported from the laterite soils of India. It is different from the placer mineral deposits in the beaches of south Kerala[27].

REE distribution in the Vembanad estuary, coastal and shelf region of Kerala and impact of rare earth mining and contamination of soil and water in the Chavara and Kollam placer mineral regions has been reported[28–32].

Geology of Kerala

Kerala is bounded by the Western Ghats (mountain ranges) in the east and the Arabian Sea in the west. Figure 1 shows the soil map of this state and the drainage basins of rivers[26,33–35]. The Archean and Proterozoic rocks occur as dominant bedrocks. Within the Proterozoic formations, Khondalite Group, Charnockite Group, Sargur Group and Dharwar Group of rocks are present. Broadly, the hinterland comprises khondalite–granulite–granite rocks intruded by large pegmatites in south and central Kerala and Archean schists and charnokites with mafic granulites in north Kerala. The Tertiary formations unconformably overlie the bedrock and extend as a narrow belt along the coast. They contain essentially variegated sandstone and clay with lenticular seams of lignite. Quaternary sediments occur in the coastal region. All these formations are covered by thick laterites. Monazite-rich heavy mineral sands occur abundantly in the beaches of south Kerala[36,37].

A humid tropical climate prevails in the region with an annual rainfall of ~3500 mm, and about 80% of the rainfall occurs only during the southwest (SW) monsoon. The eastern part of Kerala is mountainous and is characterized by forest soils in the upper region and alluvial sediments in the coastal region. Laterites largely occur between the forest soils and coastal alluvium (Figure 1). Both primary (*in situ*) and secondary (detrital) laterites occur at different topographic levels, and their composition varies from Fe-rich to Al-rich types[38]. The sediments collected at the lower reaches of 21 rivers from Kerala have been analysed in this study.

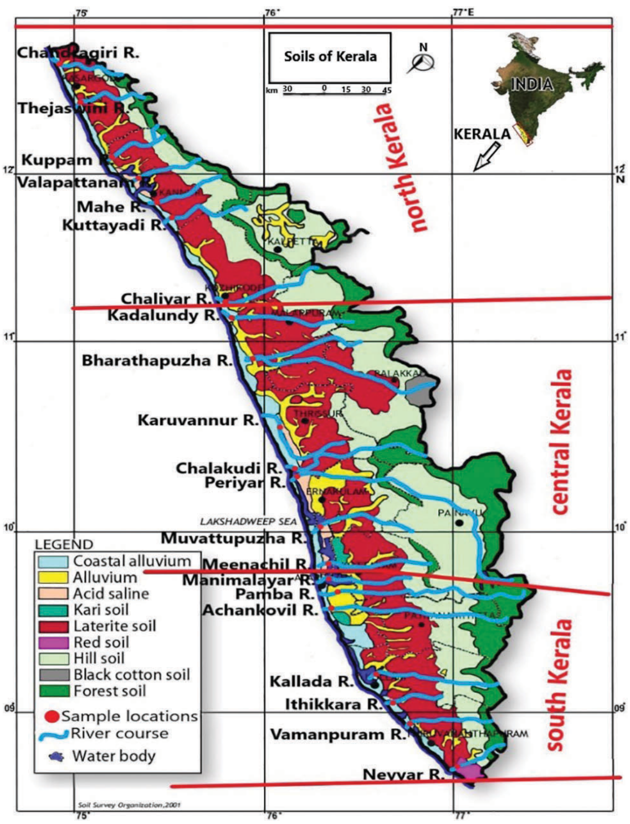

Figure 1. Rivers of Kerala from which sediment samples were collected for the present study. Soil map of Kerala, India is also shown[33].

Materials and methods

For the present study, sediments were collected at the lower reaches from the riverbeds of 21 rivers in Kerala, between the Neyyar River in the south and the Chandragiri River in the north (Figure 1). Van Veen Grab was used for sample collection. The sediments recovered were silty clay with <1% sand content. The clay (<4 μm) and silt (>4–63 μm) fractions of sediments were separated, dried at <60°C and powdered. The powders were used to determine the chemical composition. For REEs, closed acid digestion using HF : HNO_3 mixture was adopted. Detailed procedure for the preparation of sample solutions for REEs is given in Saibabu *et al.*[39]. REEs were analysed using a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS, Nu Instruments, UK) at the CSIR-National Geophysical Research Institute laboratory in Hyderabad. Tables 1 and 2 show analytical data on REEs for the clay and silt fractions respectively.

Results

Total rare earth elements and their relationship with other elements

The total REE (ΣREE) content in the clay fraction of sediments ranged from 153 to 421 μg/g, with an average value of 247.48 μg/g, significantly higher than that of the Upper Continental Crust[40] (UCC: 148.96 μg/g), Post-Archaean average Australian Shale[41] (PAAS: 208.63 μg/g) and World River Average Clay[42] (WRAC: 205.13 μg/g; Figure 2 and Table 1). The average ΣREE was low in the rivers of south and north Kerala but gradually increased to high values in the rivers of central Kerala, with the highest ΣREE corresponding to the minor (48 km long) Karuvannur River (Table 1). ΣREE was slightly higher than in PAAS in the moderately long rivers (Muvvathupuzha, Periyar, Chalakudi and Bharathapuzha) of central Kerala (Figure 2).

ΣREE of the silt fraction ranged from 206 to 1080 μg/g, with an average of 443.52 μg/g (Figure 2 and Table 2), significantly higher than in the clay fraction (247.48 μg/g) and World River Average Silt[42] (WRAS: 182.86 μg/g). Peak-high ΣREE in silt was found in south and central Kerala, with a similar trend to clay fractions in central Kerala. ΣREE was low in sediments of north Kerala (Figure 2).

ΣREE of the clay fraction of sediments showed no correlation with Al_2O_3, Fe_2O_3, K_2O and TiO_2, and moderate correlation was found with MnO and a significant correlation

Table 1. Concentrations of rare earth elements (REEs; μg/g) and trace metals (μg/g) of the clay fraction (<4 μm) from river sediments of Kerala

	River	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE	Zr	Hf	U	Th
South Kerala	Neyyar	53.240	106.825	9.930	33.437	6.552	1.617	6.238	1.064	5.841	29.972	1.161	3.378	0.471	3.336	0.532	233.622	137.120	4.086	2.607	13.655
	Vamanpuram	43.187	82.136	8.002	26.680	5.354	1.342	5.179	0.912	5.115	25.595	0.994	2.779	0.389	2.767	0.434	185.271	143.976	4.381	3.414	10.231
	Ithikkara	56.907	102.745	10.750	35.933	6.824	1.478	6.115	0.993	5.238	26.177	1.000	2.788	0.380	2.626	0.426	234.203	142.892	4.362	5.123	15.633
	Kallada	47.927	89.749	9.484	33.176	6.715	1.649	6.133	1.034	5.504	26.679	1.073	2.983	0.406	2.801	0.449	209.084	116.573	3.647	2.540	9.816
	Achankovil	57.932	111.930	11.770	41.965	7.873	2.086	6.685	1.045	5.679	28.410	1.121	3.122	0.430	3.003	0.482	255.122	133.505	4.262	2.284	11.033
	Pamba	60.309	123.480	12.408	43.289	7.786	1.756	6.264	0.916	4.749	22.730	0.919	2.540	0.342	2.342	0.385	267.485	136.808	4.412	1.786	12.712
	Manimalayar	68.458	139.004	14.139	48.626	8.498	1.863	6.852	0.990	5.100	24.622	0.974	2.734	0.370	2.541	0.418	300.568	118.321	3.804	1.601	13.452
	Range	43.187–68.458	82.136–139.004	8.002–14.139	26.680–48.626	5.354–8.498	1.342–2.086	5.179–6.852	0.912–1.064	4.749–5.841	22.730–29.972	0.919–1.161	2.540–3.378	0.342–0.471	2.342–3.336	0.385–0.532	185.271–300.568	116.573–143.976	3.647–4.412	1.601–5.123	9.816–15.633
	Avg.	55.423	107.981	10.926	37.587	7.086	1.684	6.209	0.993	5.318	26.312	1.035	2.903	0.398	2.774	0.447	240.765	132.742	4.136	2.765	12.362
	STD (±)	8.296	19.354	2.037	7.438	1.048	0.246	0.535	0.060	0.378	2.386	0.086	0.280	0.042	0.325	0.048	38.022	11.067	0.304	1.197	2.100
Central Kerala	Meenachil	44.816	85.166	9.896	35.764	6.909	1.605	5.840	0.886	4.571	21.606	0.899	2.436	0.332	2.302	0.361	201.784	179.703	5.895	4.271	12.832
	Muvattupuzha	68.289	138.708	13.864	47.097	8.371	1.715	6.661	0.970	5.124	23.608	0.970	2.700	0.367	2.536	0.397	297.771	124.706	4.264	1.934	19.216
	Periyar	94.498	177.070	18.315	61.382	10.658	2.167	8.609	1.238	6.342	29.951	1.187	3.335	0.447	3.034	0.475	388.756	136.385	4.492	1.977	24.337
	Chalakudi	80.320	148.803	17.407	62.588	11.427	2.709	8.972	1.284	6.550	30.124	1.206	3.304	0.437	2.930	0.464	348.400	143.885	4.719	1.542	11.558
	Karuvannur	95.765	179.624	21.943	78.956	13.800	3.337	10.458	1.430	7.035	32.174	1.295	3.496	0.455	3.000	0.476	421.068	146.172	4.737	1.879	9.131
	Bharathapuzha	81.695	162.440	17.850	63.995	11.376	2.653	8.854	1.249	6.228	28.920	1.156	3.174	0.423	2.859	0.450	364.402	106.617	3.833	1.694	11.354
	Kadalundy	60.331	116.003	12.989	46.436	8.607	2.135	7.129	1.065	5.466	26.852	1.075	2.957	0.400	2.746	0.448	267.787	157.007	5.258	1.927	11.897
	Range	44.816–95.765	85.166–179.624	9.896–21.943	35.764–78.956	6.909–13.800	1.605–3.337	5.840–10.458	0.886–1.430	4.571–7.035	21.606–32.174	0.899–1.295	2.436–3.496	0.332–0.455	2.302–3.034	0.361–0.476	201.784–421.068	106.617–179.703	3.833–5.895	1.542–4.271	9.131–24.337
	Avg.	75.102	143.973	16.038	56.603	10.164	2.332	8.075	1.160	5.902	27.605	1.113	3.057	0.409	2.772	0.439	327.138	142.068	4.743	2.175	14.332
	STD (±)	18.510	34.154	4.020	14.381	2.337	0.610	1.595	0.193	0.873	3.808	0.140	0.380	0.045	0.268	0.043	75.893	23.275	0.672	0.937	5.412
North Kerala	Chaliyar	35.194	74.054	8.001	29.443	5.878	1.573	5.302	0.833	4.550	22.907	0.907	2.635	0.363	2.541	0.420	171.692	119.738	4.031	1.757	7.468
	Kuttyadi	33.951	68.944	7.245	25.880	4.822	1.181	4.139	0.627	3.289	16.558	0.660	1.888	0.263	1.864	0.306	155.061	142.313	4.695	4.371	10.683
	Mahe	38.633	77.504	8.922	32.774	6.315	1.582	5.529	0.853	4.621	23.483	0.916	2.634	0.355	2.420	0.391	183.447	220.885	6.870	3.243	8.580
	Valapatanam	49.214	98.386	10.745	39.076	7.519	2.008	6.446	0.998	5.348	25.690	1.037	2.933	0.404	2.823	0.448	227.383	147.439	4.973	2.184	8.832
	Kuppam	36.712	73.597	7.931	28.753	5.652	1.448	4.972	0.772	4.095	20.398	0.815	2.304	0.314	2.173	0.361	169.899	188.309	6.097	3.113	10.304
	Thejaswini	29.485	63.296	6.865	25.806	5.633	1.619	5.475	0.932	5.380	28.056	1.105	3.215	0.451	3.211	0.534	153.007	166.687	5.497	2.226	7.098
	Chandragiri	31.472	70.088	6.950	25.633	5.438	1.467	5.262	0.909	5.355	27.743	1.102	3.256	0.463	3.335	0.552	161.281	178.631	5.827	2.473	10.401
	Range	29.485–49.214	63.296–98.386	6.865–10.745	25.633–39.076	4.822–7.519	1.181–2.008	4.139–6.446	0.627–0.998	3.289–5.380	16.558–28.056	0.660–1.105	1.888–3.256	0.263–0.463	1.864–3.335	0.306–0.552	153.007–227.383	119.738–220.885	4.031–6.870	1.757–4.371	7.098–10.683
	Avg.	36.380	75.124	8.094	29.624	5.894	1.554	5.304	0.846	4.663	23.548	0.935	2.695	0.373	2.624	0.430	174.539	166.286	5.427	2.767	9.052
	STD (±)	6.440	11.208	1.372	4.909	0.847	0.248	0.690	0.121	0.784	4.117	0.162	0.492	0.072	0.535	0.089	25.561	33.455	0.948	0.881	1.452
	Overall range	29.485–95.765	63.296–179.624	6.865–21.943	25.633–78.956	4.822–13.800	1.181–3.337	4.139–10.458	0.627–1.430	3.289–7.035	16.558–32.174	0.660–1.295	1.888–3.496	0.263–0.471	1.864–3.336	0.306–0.552	153.007–421.068	106.617–220.885	3.647–6.870	1.542–5.123	7.098–24.337
	KRAC	55.630	109.020	11.680	41.270	7.710	1.850	6.520	1.000	5.290	25.820	1.020	2.880	0.390	2.720	0.430	247.480	147.030	4.760	2.560	11.910
	STD (±)	19.957	36.471	4.243	14.845	2.362	0.519	1.546	0.184	0.851	3.762	0.147	0.403	0.054	0.380	0.061	80.352	27.292	0.851	1.004	3.966
Reference sediments	PAAS	44.560	88.250	10.150	37.320	6.880	1.210	6.040	0.890	5.320	27.310	1.050	3.070	0.450	3.010	0.430	208.630	210.000	5.000	3.100	14.600
	UCC	31.400	63.400	7.100	27.000	4.700	1.020	4.010	0.650	3.910	21.000	0.830	2.300	0.300	2.040	0.300	148.960	203.000	4.900	1.700	8.500
	WRAC	44.610	89.200	9.690	35.600	6.700	1.380	5.370	0.830	4.870	29.840	0.980	2.780	–	2.720	0.400	205.130	148.00	3.810	–	15.100

(*Contd*)

Table 1. (*Contd*)

	River	SiO_2/Al_2O_3	Fe_2O_3/Al_2O_3	CIA	ΣREE	Sm/Nd	$(\Sigma LREE)_n$	$(\Sigma MREE)_n$	$(\Sigma HREE)_n$	$(LREE/HREE)_n$	$(La/Yb)_n$	$(Sm/La)_n$	$(Sm/Yb)_n$	$(Lu/La)_n$	Ce/Ce*	Eu/Eu*	ΣREO
South Kerala	Neyyar	1.050	0.350	96.350	233.622	0.196	4.280	6.720	4.494	0.952	1.078	0.797	0.859	1.036	1.105	1.347	374.860
	Vamanpuram	1.410	0.410	94.220	185.271	0.201	3.403	5.677	3.699	0.920	1.054	0.803	0.847	1.041	1.052	1.358	300.169
	Ithikkara	1.350	0.370	95.280	234.203	0.190	4.463	6.279	3.615	1.235	1.464	0.777	1.137	0.775	0.993	1.219	362.806
	Kallada	1.350	0.410	92.230	209.084	0.202	3.916	6.573	3.848	1.018	1.156	0.907	1.049	0.971	1.004	1.369	335.408
	Achankovil	1.430	0.500	93.880	255.122	0.188	4.853	7.285	4.090	1.186	1.303	0.880	1.147	0.862	1.022	1.532	405.744
	Pamba	1.330	0.450	92.220	267.485	0.180	5.135	6.417	3.262	1.574	1.740	0.836	1.455	0.661	1.086	1.339	410.081
	Manimalayar	1.300	0.450	87.550	300.568	0.175	5.807	6.908	3.530	1.645	1.820	0.804	1.463	0.633	1.080	1.300	456.453
	Range	1.050–	0.350–	87.550–	185.271–	0.175–	3.403–	5.677–	3.262–	0.920–	1.054–	0.777–	0.847–	0.633–	0.993–	1.219–	300.169–
		1.430	0.500	96.350	300.568	0.202	5.807	7.285	4.494	1.645	1.820	0.907	1.463	1.041	1.105	1.532	456.453
	Avg.	1.320	0.420	93.104	240.765	0.190	4.551	6.551	3.791	1.219	1.374	0.829	1.137	0.854	1.049	1.352	377.931
	STD (±)	0.130	0.050	2.873	38.022	0.010	0.797	0.508	0.403	0.292	0.312	0.048	0.251	0.170	0.044	0.094	51.747
Central Kerala	Meenachil	2.010	0.400	87.340	201.784	0.193	3.904	6.008	3.136	1.245	1.315	0.999	1.313	0.834	0.975	1.346	326.691
	Muvattupuzha	1.210	0.570	93.150	297.771	0.178	5.732	6.714	3.461	1.656	1.819	0.794	1.444	0.602	1.090	1.224	453.545
	Periyar	1.230	0.450	93.240	388.756	0.174	7.576	8.479	4.193	1.807	2.104	0.730	1.537	0.521	1.023	1.205	573.542
	Chalakudi	1.370	0.480	90.600	348.400	0.183	6.881	9.207	4.099	1.679	1.852	0.921	1.706	0.598	0.958	1.425	523.594
	Karuvannur	1.400	0.540	91.400	421.068	0.175	8.462	10.657	4.255	1.989	2.156	0.933	2.013	0.515	0.952	1.480	621.029
	Bharathapuzha	1.610	0.700	91.730	364.402	0.178	7.147	8.986	3.971	1.800	1.930	0.902	1.741	0.571	1.026	1.408	545.647
	Kadalundy	1.490	0.580	95.240	267.787	0.185	5.192	7.443	3.806	1.364	1.484	0.924	1.371	0.769	0.998	1.452	424.298
	Range	1.210–	0.400–	87.340–	201.784–	0.174–	3.904–	6.008–	3.136–	1.245–	1.315–	0.730–	1.313–	0.515–	0.952–	1.205–	326.691–
		2.010	0.700	95.240	421.068	0.193	8.462	10.657	4.255	1.989	2.156	0.999	2.013	0.834	1.090	1.480	621.029
	Avg.	1.470	0.530	91.814	327.138	0.181	6.413	8.213	3.846	1.649	1.809	0.886	1.589	0.630	1.003	1.363	495.478
	STD (±)	0.270	0.100	2.491	75.893	0.007	1.558	1.599	0.413	0.261	0.309	0.092	0.246	0.123	0.048	0.110	100.398
North Kerala	Chaliyar	1.620	0.570	92.580	171.692	0.200	3.206	5.687	3.485	0.920	0.935	1.082	1.012	1.235	1.063	1.501	296.508
	Kuttyadi	2.910	0.580	31.860	155.061	0.186	2.950	4.314	2.532	1.165	1.230	0.920	1.131	0.935	1.057	1.409	255.220
	Mahe	1.630	0.550	88.260	183.447	0.193	3.502	5.840	3.358	1.043	1.079	1.059	1.142	1.048	1.009	1.427	300.043
	Valapatanam	2.760	0.820	26.950	227.383	0.192	4.325	6.934	3.833	1.128	1.178	0.990	1.165	0.943	1.027	1.537	369.291
	Kuppam	1.280	0.620	88.240	169.899	0.197	3.210	5.255	3.009	1.067	1.141	0.997	1.138	1.018	1.035	1.455	286.555
	Thejaswini	1.190	0.580	90.760	153.007	0.218	2.747	6.174	4.358	0.630	0.620	1.237	0.767	1.876	1.068	1.553	276.764
	Chandragiri	1.270	0.470	95.040	161.281	0.212	2.872	5.951	4.480	0.641	0.638	1.119	0.713	1.816	1.135	1.461	291.094
	Range	1.190–	0.470–	26.950–	153.007–	0.186–	2.747–	4.314–	2.532–	0.630–	0.620–	0.920–	0.713–	0.935–	1.009–	1.409–	255.220–
		2.910	0.820	95.040	227.383	0.218	4.325	6.934	4.480	1.165	1.230	1.237	1.165	1.876	1.135	1.553	369.291
	Avg.	1.810	0.600	73.384	174.539	0.200	3.259	5.736	3.579	0.942	0.974	1.058	1.010	1.267	1.056	1.478	296.496
	STD (±)	0.720	0.110	30.171	25.561	0.011	0.534	0.810	0.703	0.223	0.254	0.103	0.191	0.408	0.041	0.054	35.432
	Overall range	1.050–	0.350–	26.950–	153.007–	0.174–	2.747–	4.314–	2.532–	0.630–	0.620–	0.730–	0.713–	0.515–	0.952–	1.205–	255.220–
		2.910	0.820	96.350	421.068	0.218	8.462	10.657	4.494	1.989	2.156	1.237	2.013	1.876	1.135	1.553	621.029
	KRAC	1.450	0.500	86.100	247.480	0.190	4.741	6.833	3.738	1.269	1.385	0.924	1.245	0.917	1.036	1.397	389.968
	STD (±)	0.480	0.110	19.042	80.352	0.012	1.663	1.469	0.512	0.387	0.446	0.128	0.336	0.369	0.048	0.103	105.872

Chemical Index of Alteration (CIA) = $(Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)) \times 100$ (ref. 44); LREE-La to Nd; MREE-Sm to Ho; HREE-ER to Lu (ref. 53); *n*, Normalized with respect to PAAS; Ce/Ce* (Ce anomaly) – $3Ce_{CN}/2La_{CN} + Nd_{CN}$); Eu/Eu* (Eu anomaly) – $Eu_{CN}/(Sm_{CN} \times Gd_{CN})^{1/253}$; CN denotes the concentration normalized with respect to PAAS; KRAC, Kerala Rivers Average Clay (the present study); PAAS, Post-Archean Average Australian Shale[41]; UCC, Upper Continental Crust[40]; WRAC, World Rivers Average Clay[42]; REO, Rare Earth Oxides expressed in µg/g (17 elements).

Table 2. Concentrations of REEs (μg/g) and trace metals (μg/g) of the silt fraction (>4–63 μm) from river sediments of Kerala

	River	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE	Zr	Hf	U	Th
South Kerala	Neyyar	145.081	305.721	33.993	120.726	19.893	1.789	12.646	1.442	6.318	29.512	1.125	3.144	0.438	3.093	0.500	655.909	1517.055	46.231	7.467	68.508
	Vamanpuram	232.437	521.220	54.779	194.770	32.886	1.821	20.872	2.236	8.920	38.261	1.438	3.897	0.530	3.656	0.590	1080.054	2435.706	65.310	14.628	116.474
	Ithikkara	103.471	206.222	22.170	76.875	13.279	1.644	9.869	1.317	6.429	31.928	1.166	3.297	0.456	3.196	0.505	449.894	848.154	26.056	8.176	44.692
	Kallada	157.698	322.438	38.020	135.946	23.458	2.024	15.656	1.830	7.927	36.606	1.386	3.816	0.519	3.588	0.579	714.884	1166.827	35.711	9.049	74.510
	Achankovil	94.437	180.517	19.375	68.819	11.839	2.470	9.768	1.391	6.944	34.428	1.306	3.583	0.489	3.387	0.527	404.852	336.077	10.026	2.877	22.122
	Pamba	98.874	192.571	18.836	64.159	10.441	2.140	8.193	1.118	5.564	27.011	1.044	2.867	0.384	2.607	0.416	409.214	341.202	10.021	2.034	22.961
	Manimalayar	89.549	166.214	17.560	59.812	9.839	2.169	7.731	1.065	5.325	26.420	0.996	2.713	0.362	2.455	0.376	366.168	188.075	5.498	1.260	13.249
	Range	89.549–232.437	166.214–521.220	17.560–54.779	59.812–194.770	9.839–32.886	1.644–2.470	7.731–20.872	1.065–2.236	5.325–8.920	26.420–38.261	0.996–1.438	2.713–3.897	0.362–0.530	2.455–3.656	0.376–0.590	366.168–1080.054	188.075–2435.706	5.498–65.310	1.260–14.628	13.249–116.474
	Avg.	131.650	270.700	29.248	103.015	17.376	2.008	12.105	1.486	6.775	32.024	1.209	3.331	0.454	3.140	0.499	582.996	976.157	28.408	6.499	51.788
	STD (±)	51.708	126.475	13.808	50.077	8.527	0.281	4.737	0.415	1.282	4.628	0.171	0.457	0.064	0.463	0.079	257.048	807.211	22.133	4.776	37.029
Central Kerala	Meenachil	52.658	93.228	10.733	38.062	6.866	1.622	6.145	0.942	4.957	25.168	0.960	2.723	0.376	2.636	0.417	222.325	357.100	10.428	3.351	15.265
	Muvattupuzha	138.316	247.621	25.067	81.299	12.508	2.152	9.612	1.300	6.517	32.060	1.214	3.443	0.482	3.426	0.540	533.497	1134.011	32.311	3.301	43.904
	Periyar	126.997	230.148	22.670	74.245	11.982	2.339	9.416	1.315	6.785	33.802	1.272	3.541	0.485	3.364	0.533	495.093	485.161	13.850	2.372	43.315
	Chalakudi	155.639	264.109	27.850	93.550	14.608	2.991	10.992	1.464	7.139	35.025	1.321	3.615	0.488	3.347	0.519	587.633	424.150	11.909	1.742	30.563
	Karuvannur	230.883	375.927	38.751	126.652	17.655	3.557	12.787	1.612	7.563	35.981	1.353	3.694	0.492	3.328	0.529	824.783	672.778	18.170	2.221	34.773
	Bharathapuzha	125.663	220.368	22.915	78.699	12.436	2.704	9.790	1.277	6.287	30.087	1.149	3.120	0.422	2.903	0.456	488.189	393.563	11.288	1.958	23.882
	Kadalundy	88.299	160.170	17.145	60.018	10.119	2.326	8.106	1.168	6.122	30.483	1.150	3.189	0.438	3.052	0.482	361.784	392.247	11.295	2.170	15.599
	Range	52.658–230.883	93.228–375.927	10.733–38.751	38.062–126.652	6.866–17.655	1.622–3.557	6.145–12.787	0.942–1.612	4.957–7.563	25.168–35.981	0.960–1.353	2.723–3.694	0.376–0.492	2.636–3.426	0.417–0.540	222.325–824.783	357.100–1134.011	10.428–32.311	1.742–3.351	15.265–43.904
	Avg.	131.208	227.367	23.590	78.932	12.311	2.527	9.550	1.297	6.481	31.801	1.203	3.332	0.455	3.151	0.497	501.901	551.287	15.607	2.445	29.614
	STD (±)	55.741	87.935	8.740	27.528	3.378	0.625	2.094	0.212	0.835	3.665	0.133	0.342	0.044	0.296	0.046	187.364	277.712	7.815	0.635	11.935
North Kerala	Chaliyar	44.627	89.879	10.286	38.346	7.064	1.756	6.030	0.912	4.908	25.021	0.952	2.722	0.378	2.661	0.419	210.937	232.188	6.959	1.641	7.531
	Kuttyadi	44.906	88.862	10.282	38.161	7.179	1.615	5.657	0.773	3.846	19.013	0.719	2.041	0.289	2.077	0.326	206.733	515.440	14.805	4.129	11.398
	Mahe	46.458	90.835	10.217	36.824	6.725	1.636	5.880	0.897	4.826	25.161	0.946	2.764	0.375	2.579	0.411	211.372	275.663	8.279	3.357	9.539
	Valapatanam	75.872	144.654	16.078	57.568	9.975	2.176	8.414	1.203	6.228	30.435	1.193	3.324	0.459	3.219	0.512	330.874	438.491	12.331	2.349	12.423
	Kuppam	47.622	91.909	9.990	35.622	6.195	1.484	5.276	0.792	4.271	21.864	0.835	2.403	0.338	2.412	0.388	209.536	350.740	10.305	2.992	9.560
	Thejaswini	44.164	91.224	10.182	38.634	7.871	1.928	7.288	1.163	6.575	33.841	1.325	3.809	0.537	3.840	0.613	219.152	294.705	8.929	2.245	6.937
	Chandragiri	68.916	142.744	15.718	58.969	11.515	1.963	10.328	1.524	7.964	38.583	1.526	4.275	0.603	4.319	0.693	331.059	785.791	23.142	3.103	18.164
	Range	44.164–75.872	88.862–144.654	9.990–16.078	35.622–58.969	6.195–11.515	1.484–2.176	5.276–10.328	0.773–1.524	3.846–7.964	19.013–38.583	0.719–1.526	2.041–4.275	0.289–0.603	2.077–4.319	0.326–0.693	206.733–331.059	232.188–785.791	6.959–23.142	1.641–4.129	6.937–18.164
	Avg.	53.224	105.730	11.822	43.446	8.075	1.794	6.982	1.038	5.517	27.703	1.071	3.048	0.426	3.015	0.480	245.666	413.288	12.107	2.831	10.793
	STD (±)	13.301	25.962	2.788	10.186	1.944	0.240	1.832	0.273	1.461	6.913	0.287	0.793	0.113	0.815	0.132	58.393	191.285	5.532	0.822	3.785
	Overall range	44.164–232.437	88.862–521.220	9.990–54.779	35.622–194.770	6.195–32.886	1.484–3.557	5.276–20.872	0.773–2.236	3.846–8.920	19.013–38.583	0.719–1.526	2.041–4.275	0.289–0.603	2.077–4.319	0.326–0.963	206.733–1080.054	188.075–2435.706	5.498–65.310	1.260–14.628	6.937–116.474
	KRAS	105.360	201.260	21.550	75.130	12.580	2.100	9.540	1.270	6.250	30.510	1.160	3.230	0.440	3.100	0.490	443.520	646.910	18.700	3.920	30.730
	STD (±)	56.696	111.540	11.737	40.489	6.446	0.508	3.694	0.350	1.283	5.380	0.208	0.553	0.076	0.542	0.089	230.390	538.363	15.033	3.266	27.443
Reference sediments	PAAS	44.560	88.250	10.150	37.320	6.880	1.210	6.040	0.890	5.320	27.310	1.050	3.070	0.450	3.010	0.430	208.630	210.000	5.000	3.100	14.600
	UCC	31.400	63.400	7.100	27.000	4.700	1.020	4.010	0.650	3.910	21.000	0.830	2.300	0.300	2.040	0.300	148.960	203.000	4.900	1.700	8.500
	WRAS	37.800	77.700	8.770	32.690	6.150	1.188	5.190	0.819	4.950	29.400	1.019	2.970	–	3.010	0.456	182.712	445.000	11.200	–	11.800

(*Contd*)

Table 2. (*Contd*)

	River	SiO_2/Al_2O_3	Fe_2O_3/Al_2O_3	CIA	ΣREE	Sm/Nd	$(\sum LREE)_n$	$(\sum MREE)_n$	$(\sum HREE)_n$	$(LREE/HREE)_n$	$(La/Yb)_n$	$(Sm/La)_n$	$(Sm/Yb)_n$	$(Lu/La)_n$	Ce/Ce*	Eu/Eu*	ΣREO
South Kerala	Neyyar	2.010	0.440	90.450	655.909	0.165	13.304	10.343	4.187	3.177	3.169	0.888	2.814	0.357	1.066	0.601	910.949
	Vamanpuram	1.640	0.410	91.870	1080.054	0.169	21.738	15.300	5.035	4.318	4.295	0.916	3.935	0.263	1.132	0.370	1474.516
	Ithikkara	1.700	0.460	93.660	449.894	0.173	8.903	8.721	4.321	2.060	2.187	0.831	1.818	0.505	1.046	0.765	649.776
	Kallada	1.630	0.430	90.870	714.884	0.173	14.581	12.540	4.936	2.954	2.969	0.963	2.860	0.381	1.022	0.563	1005.602
	Achankovil	1.380	0.440	91.450	404.852	0.172	7.918	9.492	4.605	1.719	1.884	0.812	1.529	0.578	1.009	1.224	601.881
	Pamba	1.600	0.510	86.240	409.214	0.163	7.976	7.939	3.620	2.203	2.562	0.684	1.752	0.436	1.063	1.233	591.771
	Manimalayar	1.830	0.440	76.130	366.168	0.165	7.226	7.649	3.380	2.138	2.464	0.712	1.753	0.436	1.005	1.325	533.311
	Range	1.380–	0.410–	76.130–	366.168–	0.163–	7.226–	7.649–	3.380–	1.719–	1.884–	0.684–	1.529–	0.263–	1.005–	0.370–	533.311–
		2.010	0.510	93.660	1080.054	0.173	21.738	15.300	5.035	4.318	4.295	0.963	3.935	0.578	1.132	1.325	1474.516
	Avg.	1.680	0.450	88.667	582.996	0.169	11.664	10.283	4.298	2.653	2.790	0.829	2.352	0.422	1.049	0.869	823.972
	STD (±)	0.200	0.030	5.973	257.048	0.004	5.286	2.762	0.627	0.897	0.794	0.103	0.881	0.102	0.044	0.386	337.103
Central Kerala	Meenachil	3.120	0.660	80.220	222.325	0.180	4.315	6.261	3.568	1.210	1.349	0.845	1.140	0.820	0.937	1.331	339.256
	Muvattupuzha	1.620	0.560	88.250	533.497	0.154	10.558	9.030	4.587	2.302	2.727	0.586	1.597	0.405	1.004	1.045	764.956
	Periyar	1.760	0.480	87.100	495.093	0.161	9.681	9.199	4.587	2.110	2.550	0.611	1.558	0.435	1.017	1.173	708.318
	Chalakudi	1.460	0.490	86.610	587.633	0.156	11.736	10.660	4.582	2.561	3.141	0.608	1.910	0.346	0.946	1.257	830.628
	Karuvannur	1.570	0.590	86.790	824.783	0.139	16.653	12.144	4.633	3.594	4.686	0.495	2.321	0.237	0.929	1.261	1132.610
	Bharathapuzha	1.790	0.570	84.670	488.189	0.158	9.684	9.373	3.980	2.433	2.924	0.641	1.874	0.376	0.967	1.306	696.477
	Kadalundy	1.840	0.540	91.440	361.784	0.169	7.094	8.294	4.146	1.711	1.955	0.742	1.451	0.565	0.977	1.369	545.990
	Range	1.460–	0.480–	80.220–	222.325–	0.139–	4.315–	6.261–	3.568–	1.210–	1.349–	0.495–	1.140–	0.237–	0.929–	1.045–	339.256–
		3.120	0.590	91.440	824.783	0.180	16.653	12.144	4.633	3.594	4.686	0.845	2.321	0.820	1.017	1.369	1132.610
	Avg.	1.880	0.550	86.440	501.901	0.160	9.960	9.280	4.298	2.274	2.762	0.647	1.693	0.455	0.968	1.249	716.891
	STD (±)	0.560	0.060	3.432	187.364	0.013	3.841	1.838	0.412	0.745	1.046	0.114	0.380	0.189	0.034	0.110	245.076
North Kerala	Chaliyar	1.820	0.610	86.960	210.937	0.184	4.061	6.330	3.584	1.133	1.133	1.025	1.162	0.973	1.008	1.433	346.159
	Kuttyadi	1.530	0.370	89.790	206.733	0.188	4.050	5.591	2.755	1.470	1.461	1.035	1.512	0.752	0.994	1.350	326.611
	Mahe	1.710	0.600	89.110	211.372	0.183	4.065	6.119	3.546	1.146	1.217	0.937	1.141	0.917	1.005	1.386	339.856
	Valapatanam	1.650	0.680	89.660	330.874	0.173	6.468	8.300	4.362	1.483	1.592	0.852	1.356	0.699	0.994	1.265	506.979
	Kuppam	1.660	0.710	88.530	209.536	0.174	4.049	5.488	3.237	1.251	1.334	0.843	1.124	0.844	1.011	1.382	338.644
	Thejaswini	1.700	0.710	91.660	219.152	0.204	4.063	7.748	5.135	0.791	0.777	1.154	0.897	1.439	1.028	1.356	368.629
	Chandragiri	1.380	0.630	94.190	331.059	0.195	6.293	9.669	5.781	1.089	1.078	1.082	1.166	1.043	1.038	0.959	518.818
	Range	1.380–	0.360–	86.960–	206.733–	0.173–	4.049–	5.488–	2.755–	0.791–	0.777–	0.843–	0.897–	0.699–	0.994–	0.959–	326.611–
		1.820	0.710	94.190	331.059	0.204	6.468	9.669	5.781	1.483	1.592	1.154	1.512	1.439	1.038	1.433	518.818
	Avg.	1.640	0.610	89.986	245.666	0.186	4.721	7.035	4.057	1.195	1.227	0.990	1.194	0.952	1.011	1.304	392.242
	STD (±)	0.140	0.110	2.333	58.393	0.011	1.135	1.574	1.086	0.239	0.269	0.117	0.194	0.246	0.017	0.161	83.458
	Overall range	1.610–	0.370–	76.130–	206.733–	0.139–	4.049–	5.488–	2.755–	0.791–	0.777–	0.495–	0.897–	0.237–	0.929–	0.370–	326.611–
		2.210	0.710	94.190	1080.054	0.204	21.738	15.300	5.781	4.318	4.686	1.154	3.935	1.439	1.132	1.433	1474.516
	KRAS	1.710	0.530	88.364	443.521	0.171	8.781	8.866	4.217	2.040	2.259	0.822	1.746	0.609	1.009	1.140	644.368
	STD (±)	0.350	0.100	4.256	230.390	0.015	4.729	2.446	0.732	0.909	1.048	0.178	0.724	0.306	0.046	0.309	299.298

Chemical Index of Alteration (CIA) = $(Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)) \times 100$ (ref. 44); LREE-La to Nd; MREE-Sm to Ho; HREE-Er to Lu (ref. 53); *n*, Normalized with respect to PAAS; Ce/Ce* (Ce anomaly) – $3Ce_{CN}/2La_{CN} + Nd_{CN})$; Eu/Eu* (Eu anomaly), $Eu_{CN}/(Sm_{CN} \times Gd_{CN})^{1/253}$; CN denotes the concentration normalized with respect to PAAS; KRAS, Kerala Rivers Average Silt (the present study); PAAS, Post-Archean Average Australian Shale[41]; UCC, Upper Continental Crust[40]; WRAS, World Rivers Average Silt[42]; REO, Rare Earth Oxides expressed in µg/g (17 elements).

with P_2O_5 (Figure 3). ΣREE of the silt fraction of sediments also showed no correlation with Al_2O_3, Fe_2O_3 and TiO_2, but showed a moderate correlation with MnO and a significant correlation with K_2O and P_2O_5 (Figure 3).

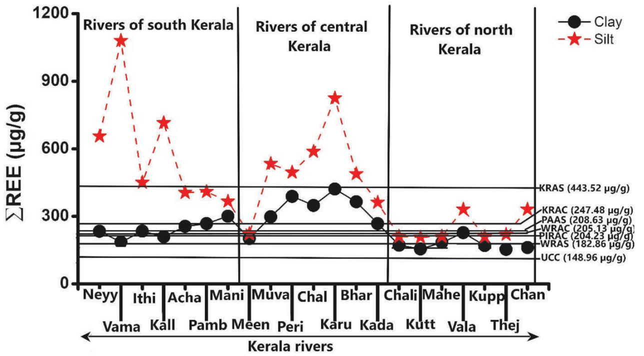

Figure 2. Total rare earth element (ΣREE) content in the clay and silt fractions of sediments from different rivers in Kerala. Neyy – Neyyar; Vama – Vamanapuram; Ithi – Ithikhara; Kall – Kallada; Acha – Achankovil; Pamb – Pamba; Mani – Manimalayar; Meen – Meenachil; Muva – Muvathupuzha; Peri – Periyar; Chal – Chalakudi; Karu – Karuvannur; Bhar – Bharatpuzha; Kada – Kadalundy; Chali – Chaliyar; Kutt – Kuttyadi; Mahi – Mahi; Vala – Valapatanam; Kupp – Kuppam; Thej – Thejaswini and Chan – Chandragiri.

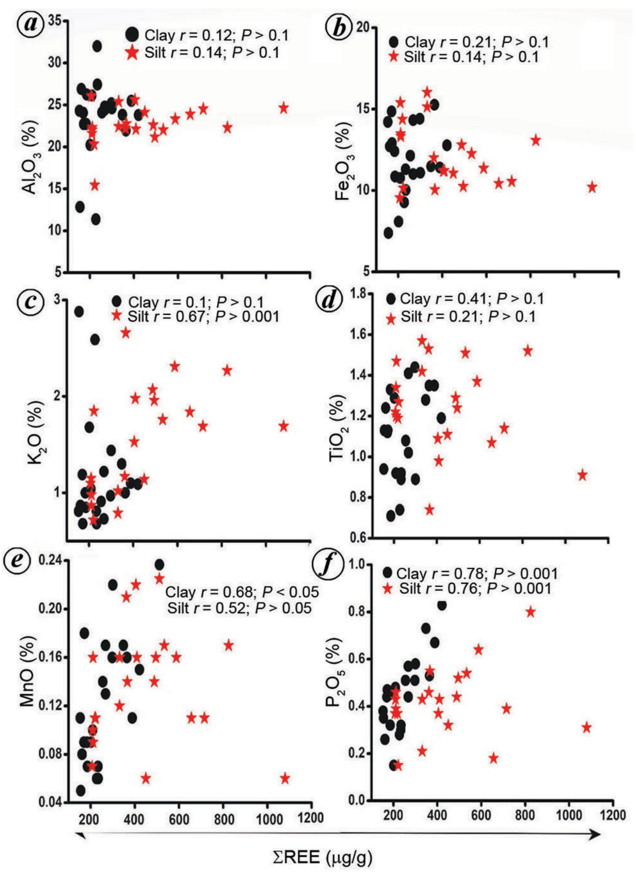

Figure 3. Correlation between ΣREE and oxides of Al, Fe, K, Ti, Mn and P in the clay and silt fractions of river sediments from Kerala.

ΣREE of the clay fraction showed no correlation with heavy metals such as Zr, Hf and U, but a significant correlation with Th (Figure 4). ΣREE, however, showed a significant correlation with heavy metals in the silt fraction.

Sm/Nd ratios

The Sm/Nd ratios ranged from 0.174 to 0.218 in the clay fractions of sediments, with relatively low values (av. 0.181) in central Kerala, followed by south (av. 190) and north Kerala (av. 0.199; Figure 5 *a*). In the silt fraction, the Sm/Nd ratios were again low (av. 0.159) in central Kerala, followed by south (av. 0.168) and north Kerala (av. 0.185). The lowest Sm/Nd ratio corresponded to the sediments of the Karuvannur River in both fractions (Figure 5 *a*). The average Sm/Nd ratio was higher in the clay (0.190) than in silt fraction (0.171), UCC (0.174) and PAAS (0.184).

PAAS-normalized REE patterns

The PAAS-normalized REE patterns exhibited Middle-REE (MREE) enrichment over Low-REE (LREE) and Heavy REE (HREE) (Figure 6 and Tables 1 and 2). Further, in the clay fraction, the LREE-enriched and HREE-depleted REE patterns were typical of sediments from south and central Kerala. In north Kerala, HREE-enriched and LREE-depleted REE patterns were characteristic of the Chandragiri and Thejaswini rivers. However, flat REE patterns with near equal proportions of LREE and HREE were found in other rivers (Table 1). The Ce anomaly (Ce/Ce*) ranged from 0.95 to 1.13 in the clay fractions, with weak negative Ce/Ce* in the sediments of central Kerala (Figure 7 *a*).

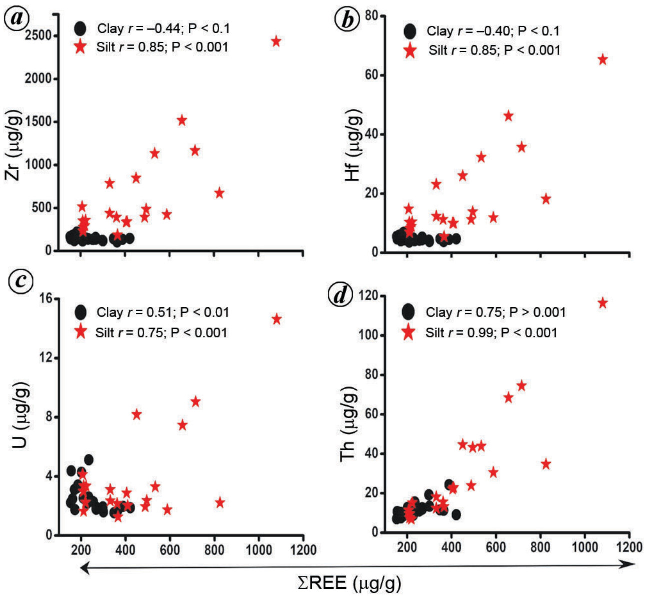

Figure 4. Correlation between ΣREE and heavy metals (Zr, Hf, U and Th) in the clay and silt fractions of river sediments from Kerala.

Positive Eu anomaly was typical of all clay fractions (Figure 7 *b*).

The silt fraction also showed LREE-enriched and HREE-depleted REE patterns in the rivers of south and central Kerala. The highest $(La/Yb)_n$ and lowest $(Lu/La)_n$ ratios correspond to the Karuvannur river from central Kerala (Table 2). In north Kerala, the Thejaswini River silt showed HREE-enriched and LREE-depleted REE patterns, while the Chandragiri River silt shows flat REE patterns with near equal proportions of LREE and HREE (Figure 6). LREE-enriched and HREE-depleted REE patterns were characteristic of other rivers. Weak positive Ce anomalies were typical in the south and north Kerala, and weak negative anomalies in central Kerala (Figure 7 *a*). The Eu anomaly was negative in the southernmost rivers and positive in all other samples (Figure 7 *b*).

Discussion

Part 1: Source sediments for REE

Lateritic REE enrichment: The REE content of river sediments is controlled largely by the composition of parent rocks, intensity of chemical weathering, and mixing and size sorting during transport[1,3,43]. The Chemical Index of Alteration (CIA) values of sediments (range: 87–95; Tables 1 and 2) indicate that the source rocks have been subjected to intense chemical weathering[44]. Under such conditions, REEs get released as soluble ions from primary REE-bearing minerals in the parent rocks and, in turn, associate with the exchangeable sites on clay minerals, oxy-hydroxides of iron and manganese, colloids and secondary phosphates[10]. No correlation of ΣREE with oxides of Al, Fe, K and Ti in the clay fractions indicates that clay minerals are not the primary hosts for REE (Figure 3). Moderate to strong correlation of ΣREE with MnO and P_2O_5 in both the clay and silt fractions illustrates that the released REEs may have been adsorbed onto the oxides and hydroxides of Mn and P (Figure 3)[1,10]. The major and trace element studies of sediments indicated low SiO_2/Al_2O_3 and Fe_2O_3/Al_2O_3 ratios (Tables 1 and 2), enrichment of Al, Fe, Ti, Mn and P, and depletion of Ca, Mg, Na and K relative to that of PAAS, suggesting that the river sediments are similar to lateritic soils[45]. In other words, the river sediments consist of intense chemical weathering products of bedrock and laterites. The correlation of ΣREE with Mn and P in both fractions

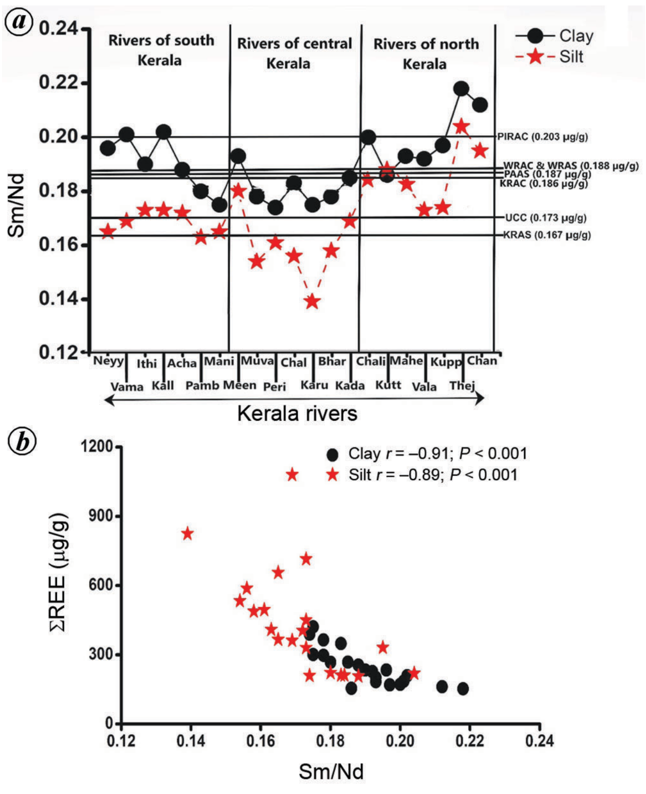

Figure 5. *a*, Variations in Sm/Nd ratios in the clay and silt fractions of sediments from different rivers in Kerala. *b*, Correlation between ΣREE and Sm/Nd ratio of the sediments.

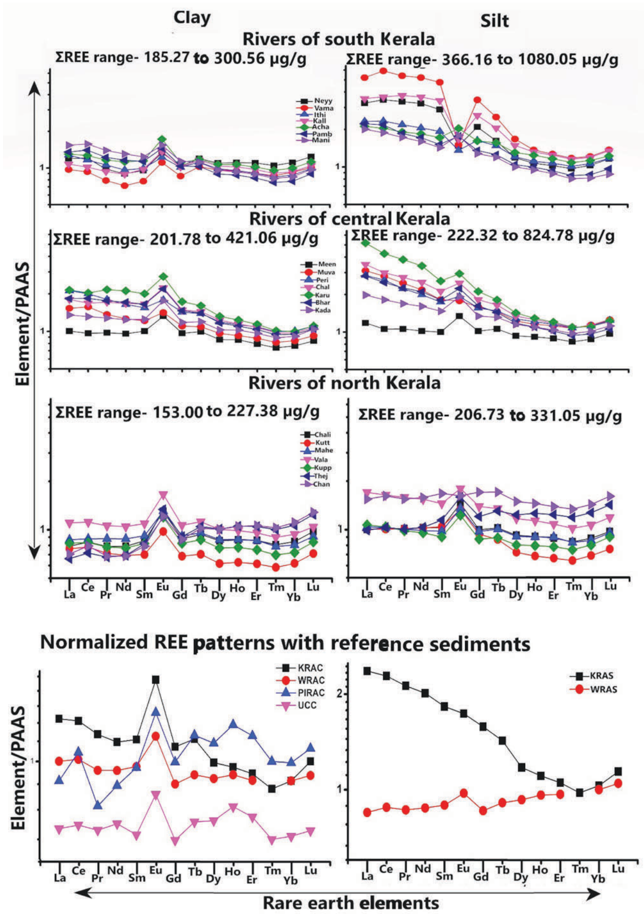

Figure 6. Post-Archaean average Australian Shale PAAS-normalized REE patterns in the clay and silt fractions of sediments in the rivers of south, central and north Kerala; KRAC, Kerala Rivers Average Clay; KRAS, Kerala Rivers Average Silt; PIRAC, Peninsular India Rivers Average Clay; WRAC, World Rivers Average Clay; WRAS, World Rivers Average Silt; UCC, Upper Continental Crust.

suggests REE adsorbed onto secondary weathering products is responsible for REE enrichment (Figure 3).

Relatively high ΣREE (Figure 2), increase in ΣREE corresponding to a decrease in Sm/Nd ratios in the sediments of central Kerala (Figure 5 *a*), and negative correlation between ΣREE and Sm/Nd ratio (Figure 5 *b*) suggest significant REE contribution is from lateritic debris. This is because a large proportion of Nd is expected to get released from REE-bearing minerals during intense chemical weathering. The Nd thus released, in turn, associates with the weathered residue, resulting in low Sm/Nd ratios. In the above, we have suggested that the weathered residue is from laterites. Therefore, high ΣREE coinciding with low Sm/Nd ratios in the sediments from central Kerala suggests that lateritic debris contributes to high REE. Ohlander *et al.*[46] reported the release of high Nd content from source rocks during intense chemical weathering and its association with the weathered residue, as a consequence, lateritic soils exhibit low Sm/Nd ratios. The highest ΣREE corresponding to the lowest Sm/Nd ratio in the size fractions of sediments from the minor Karuvannur River, central Kerala, supports the argument that the lateritic debris may not have transported the sediments over a long distance, but abundantly deposited it within the drainage basins of the river (Figures 2 and 5 *a*). Syvitski and Milliman[47] suggested that the small mountainous rivers discharge far more sediments than the estimated amount based on their drainage basin areas. The Western Ghats are at ~50–80 km from the coast in central Kerala. Therefore, it is possible that large amounts of the weathered debris brought down from the Ghats by small rivers must have accumulated within their drainage basins in central Kerala. In other words, the REE-enriched sediments associated with lateritic debris may have occupied large areas in central Kerala. Relatively low ΣREE in the clay fractions of sediments from the rivers of north and south Kerala are in accordance with the geology in the hinterland and steep gradient of the Western Ghats in the south, where clay fractions are transported further offshore.

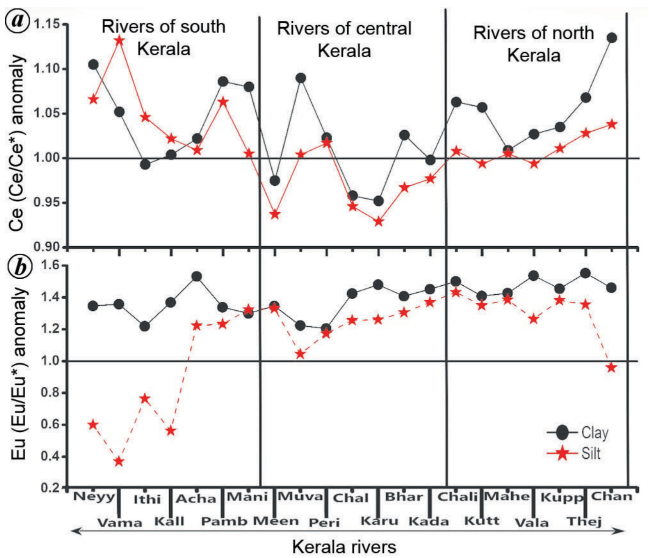

Figure 7. Variations in (***a***) Ce anomaly (Ce/Ce*) and (***b***) Eu anomaly (Eu/Eu*) in the clay and silt fractions of sediments from different rivers in Kerala.

REE enrichment from source rocks: In general, the REE content is higher in the clay than in the silt and sand fractions of sediments[3]. In contrast, low ΣREE in the clay fractions and high ΣREE in the silt fractions of sediments from south Kerala suggest different sources for REE (Figure 2). A strong correlation of ΣREE with heavy metals in the silt fractions indicates that minerals rich in heavy metals contribute to high REE (Figure 4). Heavy minerals are considered important hosts for heavy metals and REE[3]. High ΣREE and heavy metals (Zr, Hf, U and Th) content in the silts of south Kerala (Table 2) and a positive correlation between the two (Figure 4) suggest REE contribution from heavy minerals. Marchandise *et al.*[48] reported the presence of monazite, allanite, florencite, xenotime and zircon in clayey silt. Moreover, placer sands consisting of monazite, zircon, rutile, sillimanite and garnet occur abundantly in the beaches and coastal regions of south Kerala[36]. A significant correlation of ΣREE with Th and P_2O_5 in both fractions suggests that Th-bearing minerals (monazite or apatite) may have contributed to REE (Figures 3 and 4). Therefore, heavy minerals in the silt fractions contribute REE to the sediments of south Kerala (Figure 2). It is not yet known why heavy minerals or heavy metals and REE-rich silts are concentrated only in the rivers of south Kerala. It may be because khondalite rocks in the Western Ghats with steep slopes are located close to the coast in south Kerala[37,49]. Moreover, the rivers draining the Western Ghats in south Kerala are small[38]. As a consequence, the heavy minerals eroded from the khondalites are transported over short distances and deposited in rivers and coastal regions of south Kerala.

PAAS-normalized REE patterns and provenance: The normalized REE patterns provide important clues for inferring provenance composition. The MREE-enrichment over LREE and HREE is typical of clay and silt fractions (Tables 1 and 2 and Figure 6). At least three factors contribute to MREE enrichment. (a) The clay fraction usually shows higher MREE and HREE content than the bulk sediments[42]. In this study, both the clay and silt fractions exhibited high MREE content. (b) Intense chemical weathering causes MREE enrichment in river sediments[1]. High CIA values suggest intense chemical weathering in the drainage basins of the rivers and is probably a factor for MREE enrichment. (c) Phosphate usually adsorbs more MREE than LREE and HREE[7]. The positive correlation of ΣREE with P_2O_5 and MnO in both fractions indicates that phosphate and oxy-(hydr)oxide phases of Mn may have adsorbed more MREE (Figure 3)[7,11].

South Kerala: REEs fractionate during intense chemical weathering. Since LREE are less mobile than HREE, more LREE are retained with the weathering residue, and HREE is carried away as complex ions. The LREE-enriched and HREE-depleted REE patterns with negative Eu anomaly (Figure 6 *b*), high ΣREE (Figure 2) and heavy metal content (Table 2) in the silt from the four southernmost rivers indicate that their probable provenance is from felsic rocks. Because, felsic rocks are more enriched with heavy metals and rare earths than mafic rocks and contribute to the LREE-enriched and HREE-depleted REE patterns with striking negative Eu anomaly[50]. Heavy minerals are an important host for heavy metals. Mallik *et al.*[36] reported monazite-dominated placer minerals (monazite, zircon, garnet, sillimanite, ilmenite and mica) in the coastal sediments of south Kerala. We, therefore, suggest that the negative Eu anomaly may be related to heavy mineral assembly in the silt fraction. Garzanti *et al.*[51] reported that monazite, allanite, apatite, ilmenite, magnetite and micas (biotite, muscovite and vermiculite) exhibit LREE-enriched and HREE-depleted REE patterns with negative Eu anomaly. A strong correlation of REE with K_2O in the silt fraction indicates that mica or K-feldspar may have contributed to negative Eu anomaly (Figure 3).

The near-equal proportions of LREE and HREE with $(La/Yb)_n$ and $(Lu/La)_n$ ratios close to 1, and positive Eu anomaly are typical of clay fractions of the southernmost rivers (Tables 1 and 2). Such REE patterns are expected from the weathering of khondalites and granites intruded by pegmatites in the hinterland. It is likely that the weathered products from mafic rocks (basic and ultrabasic intrusions and garnetiferous gneisses) are admixed with those from the primary felsic rocks, resulting in near equal proportions of LREE and HREE.

Central Kerala: As mentioned earlier, the river sediments here are derived from lateritic soils. The laterite profiles exhibited stronger REE fractionation with LREE-enrichment over HREE and pronounced positive Ce anomaly[10,16,17,21]. The river sediments from Central Kerala indeed show enrichment of LREE over HREE in both size fractions (Figure 6) but with weak Ce anomalies (Tables 1 and 2). We suggest that the REE composition of river sediments may not reflect the total weathering process, as the weathered debris was altered and averaged during transport from the weathering site to the riverbed. The highest $(La/Yb)_n$ ratios and ΣREE corresponding to the lowest Sm/Nd ratios in both the fractions of sediments from the minor Karuvannur River in central Kerala support the argument that the weathering product from laterite is associated with the river sediments. Hard rocks are exposed in the channels of a few rivers, implying that the source rock may also have contributed to total REE, especially in the silt fractions. Source rocks in this region are charnockites and gneisses intruded by granites and basic rock types. Therefore, we suggest that the LREE-enriched and HREE-depleted REE patterns are controlled largely by the weathering products of laterites and source rocks, modified by the sedimentary processes during transport.

North Kerala: The HREE-enriched and LREE-depleted REE patterns in both fractions of sediments from the Tejaswini and Chandragiri rivers indicate the dominance of mafic material in the hinterland (Archean schists and charnockites with mafic granulites) (Figure 6). Although the sediments in the other rivers of north Kerala are marginally enriched with LREE, the ratio of $(Lu/La)_n$ tending to become 1 implies increasing proportions of the mafic component. Thorough mixing, recycling and re-distribution of fine-grained sediments during transport, especially in heavy monsoonal conditions, result in homogenization of the sediments and uniform REE patterns.

Ce and Eu anomalies: Ce is a light REE and occurs as Ce^{3+} or Ce^{4+} in oxidizing conditions. When Ce(III) is oxidized to Ce(IV) at near-surface conditions, it forms CeO_2, a stable compound in the laterite soil layer and gives rise to a positive Ce anomaly. A pronounced positive Ce anomaly has been reported in intensively weathered profiles on various source rocks and lateritic profiles[10,16]. However, the weak positive Ce anomaly in the river sediments of south and north Kerala indicates that the anomaly was altered or weakened during the transport of weathered debris in the rivers (Figure 7 *a*). Weak negative Ce anomaly in the river sediments of central Kerala suggests that the weathered debris represents either a weaker degree of lateritization or mild reducing conditions (Figure 7 *a*). Saibabu *et al.*[45] reported that the river sediments exhibit high kaolinite, followed by gibbsite and illite, suggesting sediments with early stage lateritization or lateritized soils. Sanematsu *et al.*[21] reported weak Ce anomaly in the laterite profiles and suggested that the profiles were kept in reducing conditions due to the high groundwater level where REE were mobilized. Su *et al.*[10] found remarkable positive Ce anomaly in the weathering profiles and poor or no Ce anomaly in the river sediments. They suggested that the hydraulic, sorting-induced mineral redistribution can homogenize the weathering and pedogenic alterations and weaken REE fractionation in the river sediments.

Eu anomaly in the sedimentary rocks is strongly lithology-dependent. The positive/negative Eu anomaly in the river sediments is generally attributed to the presence/absence of plagioclase or related to the sediment mineral assembly. As mentioned above, negative Eu anomaly in silt is related to high heavy mineral content and felsic source rocks in the hinterland (Figure 7 *b*). Positive Eu anomaly and HREE-enriched patterns indicate the dominance of the mafic component. The flat REE patterns with equal proportions of HREE and LREE in the sediments of north Kerala suggest reworking and homogenization of the sediments. Moreover, the moderate negative correlation between $(La/Yb)_n$ ratio and Eu anomaly suggests that the increasing felsic component decreases the Eu anomaly, which is more distinct in the case of silt fraction (Figure 8 *a*). The clay fractions showed more mafic components with a low $(La/Yb)_n$ ratio and relatively high positive Eu anomaly (Figure 8 *a*). The hinterland rocks are high-grade metamorphic rocks with charnockite and different types of gneisses, with basic intrusives and migmatites. Allen *et al.*[52] reported positive Eu anomaly for charnockites of south India. The weathering product of these formations may have contributed to the positive Eu anomaly. Mafic rocks exhibit high Sc content, while felsic rocks show high Th content. Th/Sc ratios higher than in UCC (0.72) indicate dominance of felsic component, and lower ratios indicate a more mafic component[50,53]. A strong negative correlation between Th/Sc and Eu anomaly suggests the dominance of felsic component in the silt fraction of sediments in several southernmost rivers of Kerala and the dominance of mafic component in all clay fractions and some silt samples (Figure 8 *b*).

ΣREE of the Kerala Rivers Average Clay (KRAC) was higher than in WRAC. However, the normalized REE pattern of KRAC resembled that of WRAC and UCC but differed from that of the Peninsular India Rivers Average Clay[54] (PIRAC) (Figure 6). This implies that the REE composition of KRAS is close to that of UCC. The REE pattern of the Kerala River Average Silt (KRAS) distinctly differed from that of WRAS with strong LREE-enrichment and HREE depletion (Figure 6). This difference is due to the high heavy mineral content in the silt fraction of sediments from Kerala.

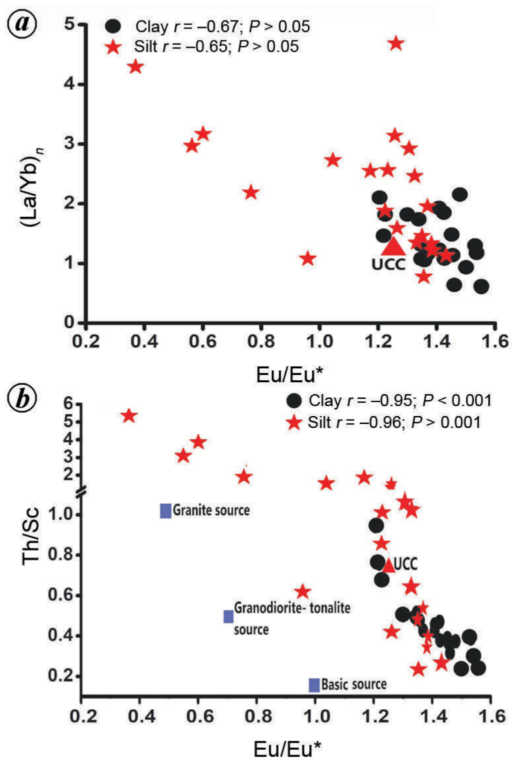

Figure 8. Correlation diagram between (***a***) Eu anomaly and $(La/Yb)_n$ and (***b***) Eu anomaly and Th/Sc ratio.

Sm/Nd ratios: The Sm/Nd ratios of sediments depend on mineral composition and their age[45]. Clays are the ultimate weathering products of rocks. High Sm/Nd ratio in the clay fractions (av. 0.19) compared to the silt fraction (av. 0.174) and UCC (0.17) suggests dominance of basic rock components. The gradual decrease in Sm/Nd ratios (to a maximum of 0.14) (Figure 5 *a*) coinciding with an increase in ΣREE in the sediments of central Kerala (Figures 5 *a* and 2) indicate that the released Nd during weathering was adsorbed onto secondary weathering products, resulting in low Sm/Nd ratios. In other words, sedimentary processes can change the Sm/Nd ratios with a high degree of fractionation. This statement contrasts with those of Viers and Wasserburg[55], and Goldstein *et al.*[56], who stated that the Sm/Nd ratios of river sediments do not change and remain close to that of UCC. On average, the Sm/Nd ratios of river sediments in south Kerala are lower than those in north Kerala in both size fractions (Figure 5 *a*). This suggests increasing proportions of mafic component in the river sediments as one proceeds from south to north Kerala. This interpretation agrees with the earlier suggestion that felsic component dominated the sediments in south Kerala, while mafic component dominated the sediments in north Kerala.

Part 2: Prospects for a viable REE deposit in river sediments

REEs are a group of 17 elements – the 15 lanthanides (La–Lu), yttrium (Y) and scandium (Sc). They exhibit high density, high melting point, high conductivity and high thermal conductance, and are extensively used in modern technology[57]. Rare earth permanent magnets (REPMs) are small, light-weight, high-strength magnets that are essential components in almost all electronic equipment, modern electric vehicles, hybrid cars, and in almost all green energy applications, aerospace and manufacture of defence equipment like missiles, rockets and guidance systems. REEs are used in the renewable energy technologies such as wind turbines, batteries and catalysts, and are often used as additives in glass fibres for fibre-optic applications and medical applications[58]. In view of different applications for REEs, their demand has been ever-increasing, with a plausible shortage in supply in the near future. Therefore, REEs are globally considered as critical and strategic elements.

REEs occur in igneous, metamorphic and sedimentary rocks. However, world resources and REE production primarily comes from igneous[59–61] (carbonatites and alkaline rocks) and sedimentary deposits[62,63] (placers, bauxites, laterites and ion-adsorption clays). Placers are the second largest resource for REE and are formed by the erosion of igneous source rocks. The placer minerals rich in REE are monazite, xenotime, ilmenite, garnet and cassiterite. Countries with notable placer deposits are the USA, Brazil, India, Malaysia, Russia, Canada and Vietnam[61]. The entire coastline of the Indian Ocean Region, i.e. the entire arc of Australia, Indonesia, Thailand, Myanmar, India, Sri Lanka, Kenya, Tanzania, Madagascar and South Africa is enriched in placer minerals[62]. At present, China, Malaysia, India, Brazil and Russia are engaged in mining and processing monazite. However, some challenges (difficult extraction and relatively expensive mining process) need to be overcome in the exploration and exploitation of REE. Moreover, extraction may harm the environment since the host minerals contain radioactive elements.

China dominates the world in reserves of rare earths and accounts for 36% of the total global reserves[64]. China produces ~90% of the global REEs, of which ~80% is exported to America. Countries in the European Union get 98% of their rare earth requirements from China. Also, China is not only a producer and consumer but also the controller of REE processing technology[65]. Since 2005, China has been threatening to withhold or restrict yearly export quotas of REE ores in order to gain control over the global market. Also, China had stopped the rare earth supply to Japan in the past.

India's status on REE and the need for exploration of new resources: The primary REE deposits that appear promising in India are the xenotime deposits in Madhya Pradesh, carbonatite–alkaline complex in Amba Dongar and Kamthai, in Gujarat, and Siwana Ring Complex, in Rajasthan[66–68], Sung Valley ultramafic alkaline carbonatite complex, West Jaintia Hills and East Khasi Hills districts of Meghalaya, and uranium, lithium, helium and REE deposits in Arunachal Pradesh[69]. Placer deposits in the beaches of Kerala, Tamil Nadu, Andhra Pradesh and Odisha, riverine REE placers in Chhotanagpur gneissic terrain and areas of Precambrian shields hold much promise for future REE exploration[60,65]. Although India shares 5.7% of the world's reserves[64], it imports most of its rare earth needs in finished form from China. This is because mining and extraction processes are capital-intensive, consume large amounts of energy and release toxic by-products. Monazite from beach placers is only mined in India for REE[67]. Indeed, India has not focused much on rare earth extraction processes. Keeping in view the recent US–China geopolitical rivalry, continuing geopolitical tension between India and China, and the global pandemic, China may threaten to withhold or stop REE supply to the US and its allies. In view of high demand for REEs, their prices are increasing rapidly in recent years. Therefore, renewed global efforts are necessary to research and develop rare earths. India needs to focus on finding new resources and processing/extraction technologies[70].

Global resources are contained in REE-bearing IADs. China is producing rare earths largely from IADs, which also occur in Thailand, Brazil, Malawi, Madagascar and the Philippines[22,23,70]. REE are also enriched in bauxites and laterites.

Here, we have documented REE enrichment in (a) clay and silt fractions of river sediments from central Kerala and (b) silt fractions of river sediments from south Kerala, the former corresponds to the weathering products of laterites and the latter being detrital and associated with heavy minerals. The monazite-dominated placer mineral deposits were reported in river sands and coastal regions of south Kerala and are being mined for REEs at present. Indeed, the REE-enriched silt fractions from south Kerala, reported here, are similar to the placer sand deposits of south Kerala. Moreover, silt in the rivers of south Kerala contains high Th content (13.2–116.4 μg/g) (Table 2), with an average of 51 μg/g, much higher than in UCC. Since Th is a radioactive material, chemical processing of silt for concentrating rare earths may give rise to thorium-rich by-products.

We propose here that REEs that are associated with the weathering products of laterites in river sediments from central Kerala are similar to IADs and may serve as a viable deposit for the following reasons:

(a) Figure 9 shows the Rare Earth Oxide (REO) content of the clay and silt fractions of sediments. The total REO content of the clay (327–621 μg/g) and silt fractions (339–1132 μg/g) of river sediments from central Kerala (Figure 9) is much higher than in the UCC[40] (239.51 μg/g), and PAAS[41] (326.81 μg/g). The ΣREO range of river sediments (327–1132 μg/g) is within that reported for IADs from China[22] (300–7000 μg/g), Madagascar[24] (300–3500 μg/g), Africa (900–4000 μg/g), Asia (300–3300 μg/g) and South America (3260 μg/g)[23]. Ram *et al.*[25] noted that the REO content of IADs varies widely from one deposit to another and exhibits a high level of inhomogeneity within a deposit. Despite the low REO content, IADs are considered economically viable because of the relatively easy recovery of REEs using low-cost leaching techniques[23]. When compared to IADs, the REO content of river clay is of low grade and within the lower end of the ∑REO range reported for IADs. Like IADs, recovery of clay from rivers is less expensive, and no mining is involved. Since REEs are adsorbed onto the weathered products of laterites in river clay, low-cost leaching techniques can produce high-grade REO products. In other words, almost no mining expenses and low processing costs are the advantages, and REEs can be extracted from river clay with ease and at a much lower cost compared to IADs.

(b) IADs exhibit both positive and/or negative Ce anomalies, whereas the river clay of Kerala exhibits weak positive or weak negative Ce anomalies.

(c) Positive Eu anomaly is characteristic of both river clay and IAD.

(d) The average Th content in the clay fractions of river sediments from central Kerala (14.3 μg/g) is close to that of UCC (8.5 μg/g) and PAAS (14.6 μg/g). Although the average Th content of the silt fractions (29.6 μg/g) of sediments from central Kerala is slightly higher than the

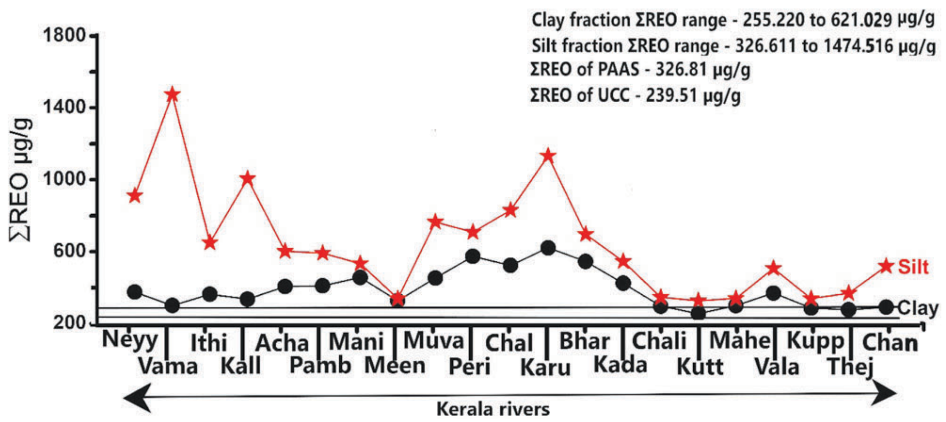

Figure 9. Total Rare Earth Oxide (ΣREO) content of sediments from different rivers in Kerala.

clay fractions, the highest ΣREE associated with the lowest Sm/Nd ratios in silt from central Kerala suggests that the REEs occur largely as adsorbed ions on weathered products of laterites, and may be easily extracted using low-cost leaching techniques. Therefore, the river clay of central Kerala may serve as a viable REE deposit.

Of the 41 west-flowing rivers in Kerala, only 21 analysed in this study. Most of the rivers in Kerala are small[38] and bring sediments from the Western Ghats (mountainous regions). The landscape of the state is covered with thick laterites (Figure 1). Therefore, there may be stronger erosion of laterites and their weathered products are not transported far away, but deposited within the river basins or on the lower slopes of the Western Ghats as secondary laterites. Therefore, detailed exploration within the sedimentary basins of the rivers from central Kerala may prove worthy of finding economically viable REE deposits. Since India is importing REEs, it is time that it should explore and focus on laterite-associated river clay for a viable REE deposit. Exploration of river sediments may provide a viable REE deposit.

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