

Mineralogical Exploration for Rare Earth Element Potential in Kalutara Coastal Areas

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Abstract

Rare Earth Element (REE) quantity is a main factor that determines the wealth of a country. The main aim of this study is to discover a new REE deposit that can contribute to the Sri Lankan economy. Calido Beach is a coastal region where Kalu-river joins the sea in Kalutara, Sri Lanka. In this study, this coastal region is divided into four divisions as Kalutara North (KN), Kalutara South (KS), Sand Spit (SS) and river delta. Beach sand (n=5) and river sediment (n=30) samples were collected covering all four divisions and analyzed for mineralogy, grain size distribution and microscopic observation for prospecting unconventional Rare Earth Mineral (REM) sources. Analysis for mineralogy of samples via X-ray Diffraction (XRD) test revealed positive availability of REMs such as Monazite (Ce), Monazite (Nd), Xenotime and Bastnasite. According to grain size distribution (GSD) test results, it was found that sediments in delta had a lesser time for sorting before deposition with relevance to beach sand. Nourishment of REMs into the shore by sea waves and other sources (Beruwala placer deposit, offshore sources) increases the amount of REM content in the study area and the minable quality of beach sand as an economically viable REE source.

Keywords: Calido Beach, Grain Count, Monazite, Particle Size Analysis, X-Ray Diffraction

1. Introduction

The reason for rare earth elements (REEs) to become significant to the technological world is that they possess unique magnetic and phosphorescent and catalytic properties [1]. REEs are extracted from REMs and more than 250 Rare Earth Elements (REMs) have been identified to

date. However, only bastnasite, monazite and xenotime are commonly processed for REEs, worldwide [2].

Monazite is a rare phosphate mineral with a chemical composition of (Ce,La,Nd,Th)(PO₄,SiO₄) [3]. It generally occurs in small isolated grains as an accessory mineral in igneous and

metamorphic rocks, such as granite, pegmatite, schist and gneiss. Generally, Monazite grains are resistant to weathering, hence they tend to accumulate in soils and sediments downslope from the host rock. When the accumulation process has taken place for a long period and the concentration is high enough, it is mined for their rare earth and thorium content [4]. Monazite is a group of several combinations of minerals. The chemical formula $(Ce,La,Nd,Th) \cdot (PO_4, SiO_4)$ implies that Cerium, Lanthanum, Neodymium, and Thorium can be substituted with one another and also substitution of Phosphate for Silica can also occur [5].

Investigating the source and depositional area of sediments is important to understand the development and behaviour of the sedimentary system [6], [7]. Revealing information of the source of the placer deposit is of utter useful, since beach deposits are dynamic due to wave actions, offshore erosions, seasonal changes and wave energy [8].

Grain size distribution (GSD) can be often used to discuss geochemical parameters of sediments [9]. Grain size is identified as a key physical property when disclosing critical information about the nature and provenance of sediments [10]. The factors that GSD depends on are the parent material, transportation medium and process, and hydrodynamic sorting [11].

The source of REMs, availability of REEs in the minerals, characterization of minerals by determining geometrical parameters, determining volume percentage of Monazite, identification of types of REEs, how they are transported to the beach, and sediment dynamics in the area are addressed through this study.

The aim of the study is to investigate the potential for an unconventional REE source that could be contributing to sustainable management of the global REE issue.

1.1 Study Area

The Kalutara North Beach, also known as Calido Beach is located in Kalutara District, 40km away from Colombo. The beach is on a spit of land extending between the sea and the Bay of Kalu River. Majority of the covering of the beach is blackish colour due to the concentrates of heavy minerals which have been transported to the beach by the action of sea waves. After further studies on the area, it was figured out that these minerals are also transported to the area along the Kalu River and then added to the sea from Kalutara river mouth. The careful observation and logical analysis of topological maps and satellite images of the area was helpful to find out the actual whereabouts of the minerals on the beach. This data will be of higher importance to decide whether these minerals are accumulated repeatedly during various seasons of the year or not. The study basically targets on the content of REMs (especially Monazite) in Kalutara beach and in the river outlet area.



Figure 1: Sampling locations of Kalutara River Delta



Figure 2: Sampling locations of KN coast



Figure 3: Sampling locations of KS coast



Figure 4: Sampling locations of Sand Spit

2. Methodology

Sample locations were pre-planned and were made into a plan by using SLD 99 coordinate system.

Samples at offshore delta region were collected using a Van Veen grab sampler from the sampling locations on the map with an accuracy level of $\pm 5\text{m}$ (Fig. 1).

Beach sand samples were collected along the coast with an offset distance of 200m – 600m parallel to the sea and 5m – 10m away from Mean Sea Level (MSL) (Fig. 2, 3 and 4). Sample size was nearly 2 kg since it required a measurable sample to minimize the error in representative sampling. A pit of nearly 30 centimeters was dug in the sampling locations and samples were collected vertically down representing horizontal strata in 1 feet depth.

All the samples were oven-dried at a temperature of 105°C for 24 hours in order to remove the moisture. Dried samples were then sieved by 2 mm sieve to remove large fragments and the rest was powdered using agate mortar and pestle. Finally representative samples for the tests were separated using cone and quartering method.

2.1 Laboratory Tests

For X-ray Diffraction (XRD) test, the heavy concentrate of the representative samples were separated using Wilfley table. Concentrates were then oven-dried at a temperature of 105°C for 24 hours and then were ground using Tema mill to make the particles finer. These samples were then fed to the XRD machinery (BRUKER D8 ADVANCE ECO X-ray diffractometer). Once test was done, REMs were filtered using the XRD operating software.

Another fraction of the representative samples was subjected to perform the Grain Count test. Few drops of provided sugar solution were applied on clean glass slides and small amounts of each sample were placed on the slides. Samples were evenly spread on the slides so that grains do not overlay on top of other grains. The slides were then kept at a dry place to get air-dried for over 24 hours. Once dried, the slides were carefully observed under optical microscope and Monazite grains were carefully identified by using colour, shape, texture and relief. Finally, volume percentages of Monazite in the samples were calculated by using enlarged views and a grid.

All representative samples were then analysed to evaluate the grain size distribution. Each sample (approximately 3g) was treated with 5ml of 30% of H_2O_2 to remove organic material and dried inside fume hood.

Few drops of dispersing agent (sodium hexametaphosphate) were then added to each sample and kept for 3 days for evaporation. Approximately 0.5g of each processed sample was then wet sieved using 1mm sieve. Pan fraction was analysed using a laser particle analyser (JNGX HMK-CD2) for the granulometer range of $0.1\text{-}1000\mu\text{m}$. GRADISTATv.8 program (Blott and Pye, 2001) was used to analyse particle size statistics such as mean, sorting, skewness and kurtosis.

3. Results

3.1 Laboratory Tests

The mineralogy of the study area can be primarily used to understand the composition of the samples, thus to ensure the availability of REMs in the area. X-ray

diffraction permits rapid approximate determinations of the minerals available in a sample.

Table 1 and 2 illustrate the availability of REMs mentioned on the left. Blue squares indicate the positive availability while white squares indicate the negative availability.

Table 1: XRD results of samples from river delta

Compound Name	KN1	KN2	KN3	KN4	KN5
Aeschynite - (Ce)					
Bastnasite - (Ce)					
Thulium Titanium (IV)					
Fergusonite -(Y)-beta, syn					
Gadolinite - (Y) (CaO)					
Gadolinite - (Y) (MgO)					
Ioparite, Th-rich, syn					
Monazite - (Nd), syn					
Monazite - (Ce), syn					
Parisite - (Ce)					
Samarskite - (Y), heated					
Thorite, syn					
Cheralite (NR)					
Xenotime - (Yb)					

Table 2: XRD results of KN samples

Compound Name	KN1	KN2	KN3	KN4	KN5	KN6	KN7	KN8	KN9	KN10
Allanite - (Ce)										
Apatite - (SrOH), syn										
Bastnasite - (Ce)										
Eudialyte										
Fergusonite -(Y)-beta, syn										
Limoriite - (Y)										
Kainosite - (Y)										
Monazite - (Nd), syn										
Monazite - (Ce), syn										
Cheralite (NR)										
Mosandrite										
Pyrochlore, syn Bismuth Iron Niobium Oxide										
Rinkite										
Xenotime - (Yb)										

3.2 Grain Count Test Analysis

Enlarged mineral grains (Fig. 5) can be used to distinguish different mineral types under a reflected microscope. By counting the number of grains of Monazite in a particular area by using its colour, opacity, shape and lustre, Monazite volume percentages were obtained as tabulated in Table 3.

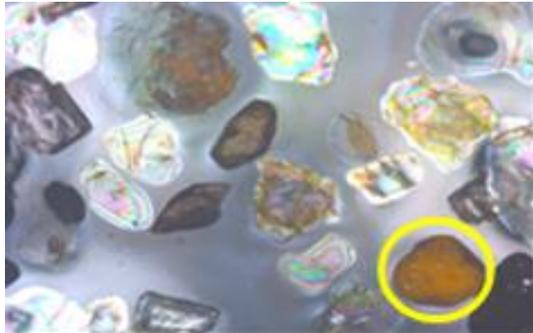


Figure 5: Enlarged mineral grains under microscope

Table 3: Volume percentages of Monazite

Sample number	Volume percentage %
KN-1	1.616
KN-4	1.212
KN-7	0.202
KS-2	2.693
KS-4	0.269
KS-9	4.369
SS-1	3.771
SS-4	1.751
SS-5	1.616
SS - 9	3.232

3.3 Grain Size Distribution (GSD) Analysis

In GSD analysis, the sediment texture is defined by evaluating its mean grain size, sorting, skewness and kurtosis.

The GSD relevant data are tabulated in Table 4, 5, 6 and 7.

Table 4: Geometric values of KN samples

Geometric Values	(μm)
Mean	306
Average skewness	-1.2
Average kurtosis	21.8
Average sorting	3.6
<i>Poorly sorted</i>	

Table 5: Geometric values of KS samples

Geometric Values	(μm)
Mean	55.4
Average skewness	-0.8
Average kurtosis	4.52
Average sorting	4.9
<i>Poorly sorted</i>	

Table 6: Geometric values of SS samples

Geometric Values	(μm)
Mean	179.9
Average skewness	-1.1
Average kurtosis	8.2
Average sorting	5.5
<i>Poorly sorted</i>	

Table 7: Geometric values of river delta samples

Geometric Values	(μm)
Mean	34.3
Average skewness	0.1
Average kurtosis	2.8
Average sorting	12.8

Extremely poorly sorted

4. Discussion

4.1 XRD test analysis

According to the XRD results, Monazite (Ce) is abundant in the delta region, but Monazite (Nd) is comparatively less available in the area. In addition to monazite, other REMs such as Xenotime are proved to be available in the delta region.

The XRD results of KS and SS locations are almost similar to that of KN results. In the three locations of KN, KS and SS, samples consist of Monazite (Nd), but no Monazite (Ce), the exact opposite scenario of samples taken from delta region. Therefore, it is clear that Monazite (Nd) is being transported to the coast from offshore sources and/or from longshore currents, not from the river outlet.

As it can be clearly seen on the tables, XRD results has proven that the study area consists of many other REMs in almost all the sampling locations on the map other than Monazite.

4.2 Grain count test analysis

Microscopic observations of the samples show that Monazite volume percentage is relatively high along Kalutara southern coast with relevant to KN, SS and river delta regions. The reason behind this can be the direction of sediment transportation along the beach. As illustrated in figure 6, the sediments were transported towards

southern coast during the monsoon during which samples were collected. Hence, monazite minerals were found comparatively in higher percentages towards southern coast.



Figure 6: Sediment transportation along the coast

But in overall consideration of monazite volume percentages resulted, it can be concluded that the percentage values are not up to minable quantities.

4.3 Grain Size Distribution (GSD) Analysis

The GSD curves of samples collected from KN, KS and from SS lies in a range of approximately 10 - 1000 μm . Mean grain size varies in the range of 55.4 - 306 μm . All the sand samples in above three locations demonstrated a transition from poorly to very poorly sorted according to [12]. Sand particles are poorly sorted to a certain extent by wave action.

Skewness is a measurement of the asymmetry of GSD in sediments. Negative skewness (coarse skewness) means a symmetrical curve with excess coarse materials. This indicates non-depositional areas with high energy conditions (high wave velocities), under which sediments are transported. Positive skewness (fine skewness) indicates depositional areas and a mixture of coarse and fine skewness indicates flux state in the area [13]. KS, KN coasts and the SS showing negative skewness values indicate that the coast is a non-depositional region. The reason for this might be the high energy waves that

sweeps the coast under which minerals keep washing away from the coast.

GSD of sediment samples collected from river delta region are quite different than those of beach sand samples. Mean grain size is quite low than in the coast, 34.3 μ m. Samples from delta region demonstrate an extremely poorly sorted condition. This indicates that sediments in the delta region are lacking time to get sorted due to its mixed and messy environment. In addition to that, wave energy in delta region is low, compared to the onshore region, which results poor sorting. Also fresh sediments keep getting added to the delta from Kalu river mouth constantly. Due to above reasons, sediments in the delta are extremely poor sorted. Positive skewness means a symmetrical curve with excess fine materials. This indicates a depositional area with low energy condition (low wave velocities), under which sediments are transported. Extremely poor sorted fine skewed sediments in the delta area exhibit the nature of material deposition through solid suspensions.

5. Conclusions

By the studies carried out based on the terrain, it can be concluded that the sources for above REMs could be Kalu River, Beruwala placer deposit and some offshore sources. According to XRD results, there are many types Rare Earth Minerals available in coastal and river outlet areas in Kalutara. Monazite (Ce) is observed in river delta region while Monazite (Nd) is observed along coastal area, abundantly. Therefore, it can be concluded that source for Monazite (Ce) can be Kalutara river outlet while sources for Monazite (Nd) can be offshore sources and sediments transported along with long shore currents.

As per the grain count results, it can be concluded that Monazite content in the study area is quite low as a percentage. But, according to the variation of the

percentage, Kalutara southern coast is showing higher Monazite volume percentages at many sampling locations with respect to other sampling locations. This is due to sediment transportation by long shore currents towards Kalutara southern direction. Samples were collected during north eastern monsoon, which further proves the fact that long shore currents were drifted towards south.

According to the geometric values obtained by particle size analysis test, skewness values have taken a negative value for the samples taken from coastal area. This concludes that coastal area is an unfavorable environment for sediment deposition. The deposit keeps forming and eroding due to wave actions throughout the year. Therefore, it can be concluded that this is a temporally varying deposit, hence availability of REMs throughout the year cannot be guaranteed.

The sorting condition of sand samples obtained from coasts was observed "Poorly sorted" while that for sediment samples obtained from river delta was observed "Extremely poorly sorted". It can be concluded that sand on the coast get sorted due to constant wave action, therefore more sorted comparatively to the sediments in the delta. Another reason for above condition is that river delta is constantly getting fed by fresh, unsorted sediments from the river and get accumulated in the calm, still environment in delta without subjecting to a sorting process. This implies that delta is a favorable depositional area.

Acknowledgements

The authors wish to acknowledge the financial support provided by the Accelerating Higher Education and Development (AHEAD) Operation of the Ministry of Higher Education of Sri Lanka funded by the World Bank (AHEAD/DOR/6026-LK/8743-LK).

Authors are also thankful to academic and non-academic staff of the Department of Earth Resources Engineering, University of Moratuwa for facilitating this study. The humble gratitude is extended to Eng Nadeera Batapola for her support for this study. Assistance from Ranjani Amarasinghe and Sandun Udayanga for field and laboratory work is also appreciated.

References

- [1] Balaram, V. (2019). Geoscience Frontiers Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*, 10, 1285–1303.
- [2] Dushyantha, N., Batapola, N., Ilankoon, I., Rohitha, S., Premasiri, R., Abeysinghe, B., et al. (2020). The story of rare earth elements (REEs): occurrences, global distribution, genesis, geology, mineralogy and global production. *Ore Geology Reviews*, 103521.
- [3] Gupta, C. K., & Krishnamurthy, N. (2005). *Extractive Metallurgy of Rare Earths* CRC Press. Boca Raton, Florida, 65, 70–75.
- [4] King, H. M. (2017). REE: Rare Earth Elements and their Uses. *Geology.com-Geoscience News and Information*.
- [5] Zhu, X. K., & O’Nions, R. K. (1999). Monazite chemical composition: some implications for monazite geochronology. *Contributions to Mineralogy and Petrology*, 137(4), 351–363.
- [6] Ratnayake, A. S., Dushyantha, N., De Silva, N., Somasiri, H. P., Jayasekara, N. N., Weththasinghe, S. M., et al. (2017). Sediment and physicochemical characteristics in Madu-ganga Estuary, southwest Sri Lanka. *Journal of Geological Society of Sri Lanka*, 18(2), 43–52.
- [7] Dushyantha, N. P., Hemalal, P. V. ., JAayawardena, C. ., Ratnayake, A. ., Premasiri, H. M. ., & Ratnayake, N. P. (2017). Nutrient Characteristics of Lake Sediments around Eppawala Phosphate Deposit, Sri Lanka. *Journal of Geological Society of Sri Lanka*, 18(2)(August), 33–42.
- [8] Amalan, K., Ratnayake, A. S., Ratnayake, N. P., Weththasinghe, S. M., Dushyantha, N., Lakmali, N., & Premasiri, R. (2018). Influence of nearshore sediment dynamics on the distribution of heavy mineral placer deposits in Sri Lanka. *Environmental earth sciences*, 77(21), 737.
- [9] Dushyantha, N. P., Hemalal, P. V. A., Jayawardena, C. L., Ratnayake, A. S., & Ratnayake, N. P. (2019). Application of geochemical techniques for prospecting unconventional phosphate sources: A case study of the lake sediments in Eppawala area Sri Lanka. *Journal of Geochemical Exploration*, 201, 113–124.
- [10] Zhangl, Q. (2016). Geochemistry of sediments from the Huaibei Plain (east china): Implications for provenance, weathering, and invasion of the Yellow River into the Huaihe River. *Journal of Asian Earth Sciences*, 121, 72r83.
- [11] Watson, E. B., Pasternack, G. B., Gray, A. B., Goñi, M., & Woolfolk, A. M. (2013). Particle size characterization of historic sediment deposition from a closed estuarine lagoon, Central California. *Estuarine, Coastal and Shelf Science*, 126, 23–33.

- [12] Folk, R. L., & Ward, W. C. (1957). Brazos River bar [Texas]; a study in the significance of grain size parameters. *Journal of Sedimentary Research*, 27(1), 3-26.
- [13] Maity, S. K., & Maiti, R. (2017). *Sedimentation in the Rupnarayan River: Volume 1: Hydrodynamic Processes Under a Tidal System*. Springer.