Diagnosis of REE Elements (La, Ce, Sc, and Y) in the Surface Sediment of the Persian Gulf

Mehri Rezaei[1], Ali Mehdinia[1]*, Abolfazl Saleh[1], Soroush Modabberi[2]

1- Department of Marine Living Science, Marine Science Research Center, Iranian National Institute for Oceanography and Atmospheric Science, P.O.Box: 141155-4781, Tehran, Iran

2- Department of Geology, Faculty of Science, University of Tehran, P.O.Box: 14155-6455, Tehran, Iran

Abstract

The distribution of some rare earth elements (La, Ce, Sc, and Y) in the sediment samples, collected form 56 stations in the offshore of the Persian Gulf during the Persian Gulf and Gulf of Oman Oceanographic Cruise (PGGOOS) in 2012, was studied. The elements were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The result revealed that the concentration of Ce (82 µg g-1) was the highest, and La lowest (0.01 µg g-1). The average concentrations of elements were 11.7, 5.6, 5.4 and 3.5 µg g-1 for Ce, Y, La and Sc, respectively. Enrichment factors (EF) indices showed the enrichment for Ce, while the other elements had EF<1. The concentration ratios of La/Sc (1.6) and Ce/La (2.1) indicated redox status of the surface sediments in the studied region of the Persian Gulf.

1. Introduction

The rare earth elements (REEs), are a group of elements that have similar crystal ionic radii and valance state. They are an ideal group to indicate the sources of the lithogenous part of marine and non-marine sedimentary deposits, e.g., mafic, felsic-igneous and sedimentary rocks Piper and Bau 2013). REEs have strong binding affinity with soil, low mobility, low natural backgrounds in soils, and non-toxic character. Accordingly, they have been reported as a potential pollution tracer. REEs range

---

* *Email: mehdinia@inio.ac.ir*

from La-Sm is classified as light rare earth elements (LREE) and Gd-Lu is considered to be heavy rare earth elements (HREE). The LREEs typically exhibit greater abundances than the HREEs (Cruse et al., 2000, Castor and Hedrick., 2006, Liu et al., 2011, Aide and Aide., 2012, López-González et al., 2012, Antonina et al.,2013). In sedimentary systems REE patterns are influenced by diagenetic processes and depositional environment. Because these elements are sensitive indicators of magmatic differentiation, they are valuable in geochemical evolution studies of the Earth. Distributions of REE alter as a function of depth, latitudinal gradients, fluctuation in water chemistry, uptake of REE by organic and oxy-

hydroxide grain coatings (Cruse et al., 2000). They are also influenced by their parent materials, weathering and pedogenic processes, texture, organic matter contents, reactivity, and anthropogenic disturbances (Aide and Aide., 2012, Kaminskas and Bitinas., 2013). REEs have been distinguished neither as essential elements nor as strong ecotoxic elements (Wang and Liang, 2015). Despite the global significance of REEs, their distribution in the surface sediments of the Persian Gulf is still unknown. It is important to investigate the environmental presence of REEs and their potential harmful effects. This study investigates the distribution and enrichment factor of some REEs (La, Ce, Sc, and Y) in surface sediments of the Persian Gulf and sees whether the high REEs concentration contaminated the surrounding environment and leading severe environmental deterioration.

2. Materials and Methods

The Persian Gulf is a relatively shallow, semi enclosed body of water, with the average depth of 35 m. The bottom topography of the Persian Gulf is mostly flat and featureless and dominated by soft sediments (Agah et al., 2012).

The sediments in the Persian Gulf have three origins: biochemical sediments including benthic fauna particles, clastic sediments discharge via rivers and the wind and chemical sediments as carbonate mud and ooids (Dehghan Chenari and Lak., 2014). The study area is restricted to the Iranian offshore waters along the northern part of the Persian Gulf. In order to cover more area, 56 stations in 15 transects at a distance of approximately 25km from each other were selected (Figure 1).
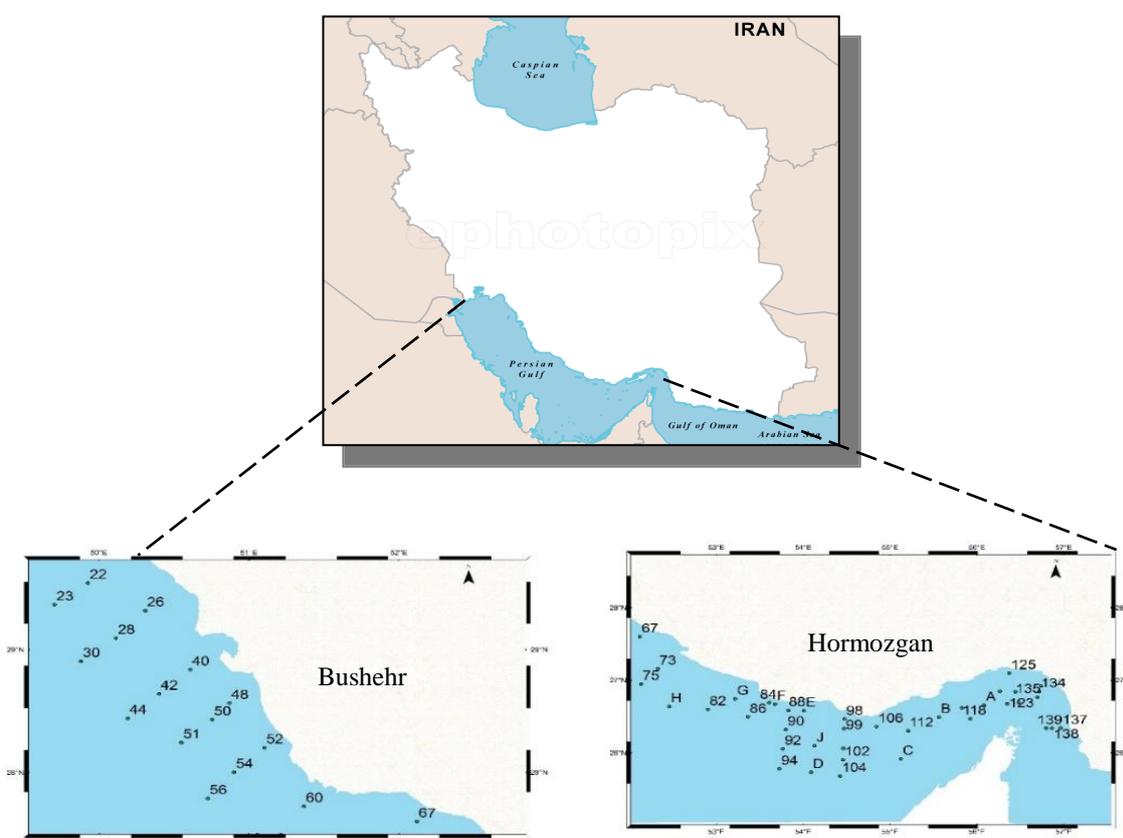

Fig. 1: The map of the studied area and sampling stations

14

This study was conducted in 2012 on the offshore and the minimum distance from the Iranian coastline was 8 kilometer.

All procedures including sampling and the sediment preparation were carried out according to the ROPME criteria. The sediment samples were taken by using Van Veen Grab. All specimens were stored in the cleaned polyethylene containers and immediately transferred to the Freezer, and kept at -45 ℃. All elements (La, Ce, Sc, and Y) were measured by using 1:1:1 Aqua Regia digestion solution and ICP-MS (Perkin-Elmer ELAN9000) in ACME lab – Canada. Detection limits for measured elements were La (0.5 µg g-1), Ce (0.1 µg g-1), Sc (0.1 µg g-1), Y (0.01 µg g-1). ACME Labs is accredited for total metals analysis under ISO 17025:2005 with the Standard Council of Canada (ACME Labs, 2014). The QA/QC included the analysis of two standard reference materials (STD DS10 and STD OREAS45EA) and a spike blank (BLK). Grain size analysis was carried out by using Horiba Laser Particle Size Analyzer LA-950. For this purpose, 25 mL of tetra-sodium-diphosphate-decahydrate 3% was added to 0.5 g the homogenized sample and transferred to the beaker, and were shook by a magnet for 2h. Loss on ignition (LoI) method was applied for carbonates and organic matter determination. For this purpose, 4 g sample was dried in an oven at 550 ℃ for 4 h. Then, the samples were weighed and dried again at 950 ℃ for 2 h till all the carbonates removed. Finally, the carbonate content was calculated by difference in sample's weight.

Statistical analyses were performed with SPSS 23.0 software. One-way ANOVA of variance with the 95% confidence interval followed by a Tukey test accepted to check the differences between the concentrations of elements in different stations. Spearman correlation and regression analysis were used to test the relationships between sediments characteristics and metal concentrations.

2.1. Enrichment factor:

Enrichment factor widely used to estimate the anthropogenic impact on soil and sediment. REE enrichment factors (EFs) were calculated for each site and each element by using the equation (Essien et al., 2009):

$$EF = \frac{[M]/[Sc])\ sample}{([M]/[Sc]\ background}$$

Where: [M] = total trace element concentration measured in soil samples (mg kg-1) and [Sc] = total concentration of Sc as the reference element (mg kg-1). The background concentration of the element was chosen from carbonate sedimentary background. According to EF classification, EF<1 is classified in the range of uncontaminated. Whereas for EF>1, it is suggested that the sources are more likely to be polluted by anthropogenic sources.

3. Results

All elements concentrations (Mean± Standard Deviation, Min and Max) and the value of each element in average shale, upper crust and carbonate sediment value are presented in Table 1. Obviously, all the elements have less value than the average shale and upper crust values. Sc and Ce had the least (0.6 µg g-1) and highest (19 µgg-1) concentrations among the other elements, respectively. The average concentrations for the selected elements were La (5.4 µg g-1), Ce (11.7 µg g-1) Sc (3.5 µg g-1) ,Y(5.6 µg g-1). All elements in sediments were lower in content than those reported worldwide for shale, upper crust, and carbonate sediment by Li and Schoonmaker.,2005; Turekian and Wedepohl., 1961 (Fig. 1). As it can be seen in Table 1, the average concentrations of the REEs in the Persian Gulf is close to the average values in the carbonate

sediments, but are less than all other values. Moreover, the textural parameters analyzed reveal that the sediments are dominantly silt - loam types. The mean carbonate content was 26.8 µg g-1. TOM contents fluctuated between 4-18 %.

Lanthanides were divided into two groups, lower atomic number (LREEs) and higher atomic number (HREEs). All measured REEs, grouped in LREEs but, Yttrium was generally classified as HREEs, because of chemical similarity (Wang and Liang,

2015). In studied areas, Ce and Sc showed higher concentration. Ce is most abundant REEs (Wang and Liang, 2015) and we found it in relatively high concentration compared with other REEs in the surface sediment of the Persian Gulf.

The correlation coefficient between elements showed that there is a statistically significant positive correlation ($p < 0.05$) between all the examined elements REEs and clay (Table 2).

Table 1: The measured elements in the surface sediment of the Persian Gulf (µg g-1)

Element	Mean±Sd	Min	Max	CV%	Average shale (Li and Schoonmaker 2005)	Upper crust (Li and Schoonmaker 2005)	Carbonate sediment (Turekian and Wedepohl, 1961
CaCO$_3$	26.8±10.5	0.0	53.72	39.4	-	-	-
TOM	11.5±2.8	4.5	18.00	25.04	-	-	-
Sand	23.4±20.2	0.0	76.08	86.58	-	-	-
Silt	69.11±19.6	19.14	98.47	28.3	-	-	-
Clay	5.39±4.4	0.0	18.01	83.11	-	-	-
La	5.48±1.6	1.0	8.40	29.7	43	30	x
Y	5.6±1.8	1.25	9.52	33	26	22	30
Ce	11.74±3.6	2.3	19.1	30.6	82	58	11.5
Sc	3.5±1.4	0.6	8.4	42.5	13	14	1

Table 2: Correlation coefficients between REEs and TOM, Carbonate and grain size

	Sand	Silt	Clay	Depth	TOM	CaCo3	La	Sc	Y	Ce
Sand	1.000									
Silt	-.795**	1.000								
Clay	-.388**	-.031	1.000							
Depth	.090	.096	.026	1.000						
TOM	-.197	.049	.328*	-.106	1.000					
CaCo3	.370**	-.106	-.601**	.069	-.556**	1.000				
La	-.467**	.179	.553**	-.365**	.517**	-.765**	1.000			
Sc	-.531**	.283*	.558**	-.267*	.524**	-.796**	.943**	1.000		
Y	-.471**	.264*	.415**	-.368**	.479**	-.727**	.928**	.946**	1.000	
Ce	-.481**	.189	.583**	-.329*	.548**	-.784**	.991**	.956**	.918**	1.000

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)
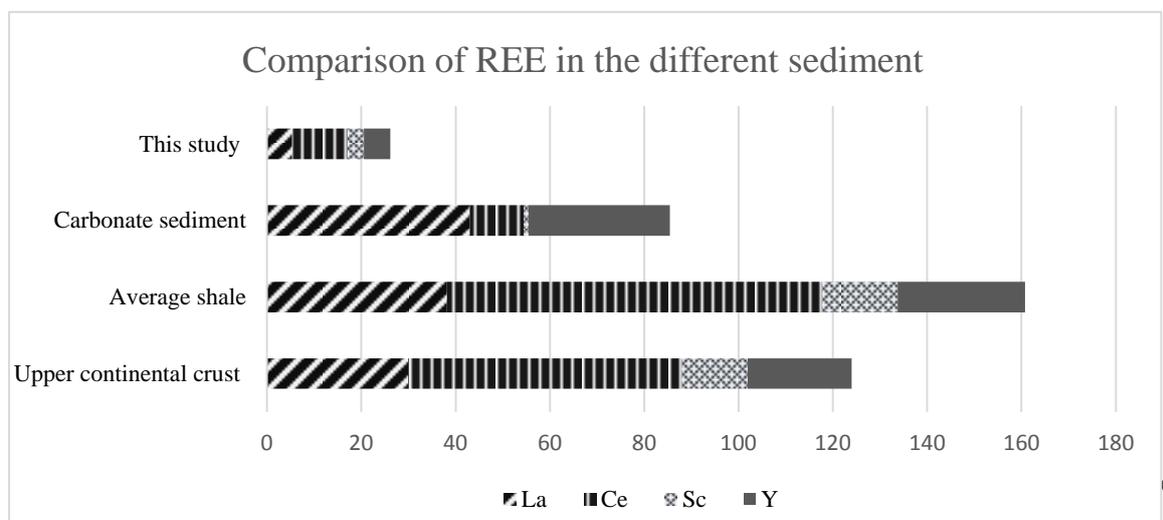
Fig. 2: REEs in comparison with their concentration in Upper Crust, Shale, Carbonate Sediments value

Low CV values indicated that REE concentrations are spatially homogeneous, whereas high CV values corresponded to a non-homogenous concentration of elements (Wang and Liang., 2015). The variances of selected elements were low varied in a range 29.7-42.5%., CVs (>30%), suggesting that their distributions might be affected by anthological source (Yan et al., 2018)

3.1. Enrichment factor

Among the selected elements, Ce has EF value of 1.05, and other elements have EF values smaller than 1. Station 40 in Bushehr province showed the highest EF for Y (0.27), Ce (1.6) and La (0.2). Enrichment factor of1 69 was observed for Sc in the station of 133 in the east of Hormozgan. This station is located near the Minab river mouth and affected by its input. The number of stations which have EF > 1 for the selected elements was: Zero for Y, 33 for Ce33, 18 for Sc and 0 for La. Sc showed the enrichment only in Hormozgan province. Actually, all stations which are situated in the east of Hormozgan showed

enrichment in Sc. Ce enrichment was observed mostly in 88% of stations located in Bushehr province. Some REEs, such as La and Ce are released into the environment from anthropogenic sources such as industrial and urban effluents, coal-burning, and application of fertilizers in agricultural fields (Özaytekin and Uyanöz., 2012).

3.2. Mapping in GIS

To better understanding of the spatial distribution of REE concentrations, mapping of enriched elements (Ce and Sc) performed in Geographical information system (GIS) (Figure 3).

The pattern of REE distribution shows geographical trend and these elements decreases with increasing distance from the coastal line which suggests terrestrial source of selected REEs elements in the Persian Gulf. The only part which show low risk near the coastal line is located around the station F. This location is rich by carbonate and calcium which act as a dilution material for elements. As well as there are not any significant activities around this area.
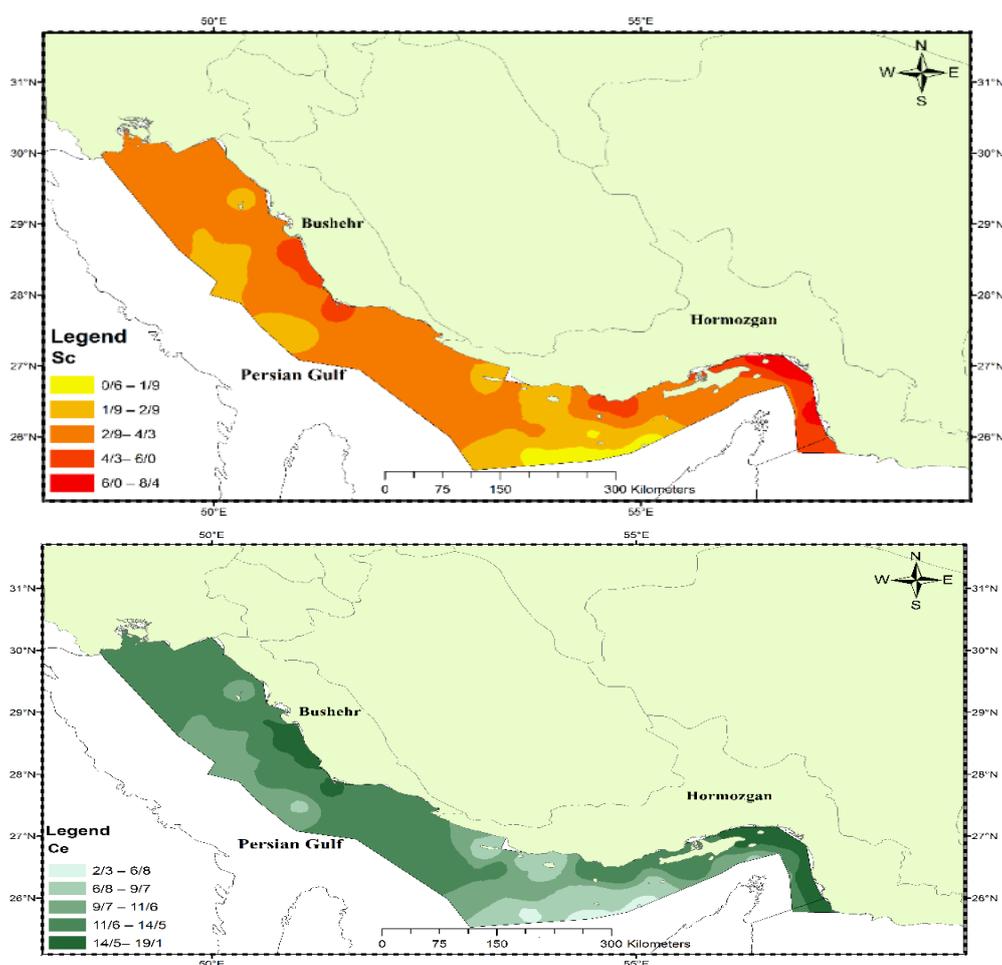
17

Fig 3: Map of REE concentration in the surface sediment of the Persian Gulf.

3.3. The Cluster Analysis (CA) and factor analysis

The main purpose of cluster analyses is categorize objects based on similarities (Suresh et al., 2012) HCA was performed in the normalized data set through squared Euclidean distances as a measure of similarity and Ward's method. The derived Dendrogram is shown in figure 4. Based on HCA, stations classified into 3 main clusters. There were 11 stations in cluster 1,15stations in cluster 2, and 30 stations grouped in cluster 3. The mean concentration of REEs in cluster 3 was higher than those in the other clusters. The majority of stations that located in Bushehr Province concentrated in cluster 1 and 2 and considerable number of

Hormozgan province's station classified in cluster 3. Accordingly, it seemed that the location of stations is important factor in REEs concentration. In Bushehr province, there are two main oil industrial zones (Asaloye and Kangan Harbour) and petrochemical &refinery unit in Khark Island which could impac on pollution discharge to the Persian Gulf. Also, in Hormozgan province there are two refineries , chromium mines, power plant and two docks which discharge their waste water to the Persian gulf. Althought studies on distribution of REEs in environment affected by different industries are scarce, it is expected to have more REE concentration in nearbay of such activities. Regarding to Fiket et al ,2016 the concentration of

18

REE decrease with increase distance form termal power plant which can be refer to the impact of this activity in REEs concentration. Additionally, different sediment texture leads to have different element content. In the east of Hormozgan (near the station of 133) sandy- mud sediment are dominant while in the west of Hormozgan (site F) a sandy texture was observed. This difference surely has profound impact on heavy metal absorption by sediment which should be considered carefully.
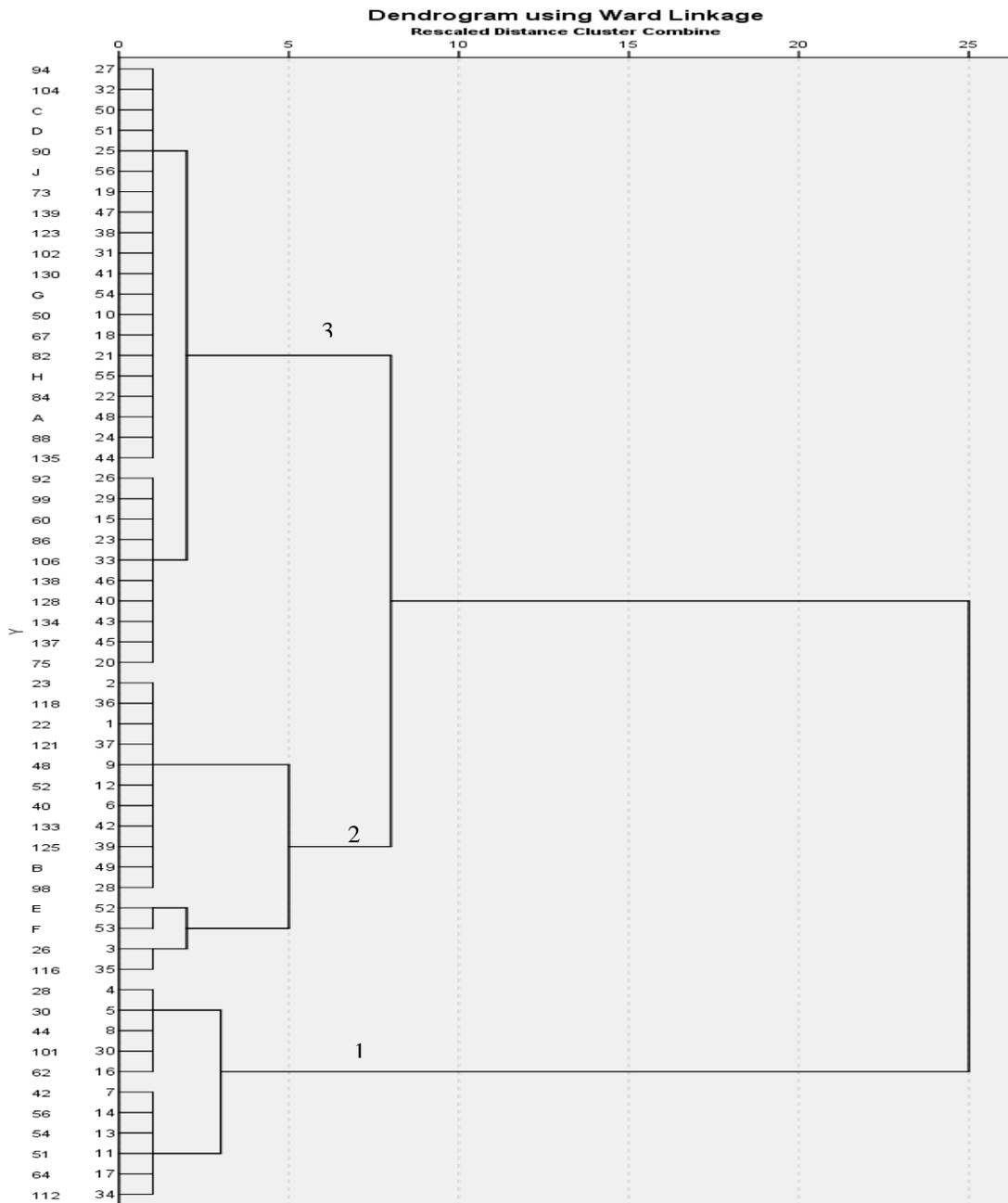

Fig. 4: Dendrogram of the sampling stations with the measured elements

19

4. Discussion

4.1. REEs ratio

Element ratios such as La/Sc are useful in the study of the chemical composition of the source rocks (Piñán-Llamas and Escamilla-Casas., 2013, Armstrong- Altrin and Machain-Castillo., 2016). La /Sc obtained as 1.6 which is below the felsic (2.5 - 16.3), upper crust (2.21) and average shale (2.4). The average La /Sc ratio in Bushehr (1.7) was much higher than Hormozgan (1.5). This ratio is less than the ratio which other authors presented in different part of the world. As well as, Ce/La ratio determined as 2.1 and the maximum ratio was observed in station G (2.3) in Hormozgan. This ratio remains mostly constant between stations, and there is no significant difference between two provinces in terms of this ratio. This ratio is an indicator of redox condition in the sediment, and get high in most oxygenated condition. The anoxic condition of bottom of the Persian Gulf was reported in some articles (Karbassi and Bayati., 2005).

Geology of studied area is affected by Zagros, Central Iran and Makran Zone. These zones are rich in dolomite, volcanic rock, and pelagic carbonates respectively (Abbaslou etal.,2013), which are known as major deposit of REEs elements (Castor and Hedrick., 2006). Regarding to Lak and Mohammadi 2013, wind delivered and biojenic sediment are dominant in north side of the Persian Gulf from Hormoz strait to Bushehr Province. Dry deposition is an important pathway for transportation of natural and anthropogenic materials from the continent to the seas, but there is no estimation about dry deposition in the sediment of Persian Gulf. Beside natural source, direct discharging of waste and waste water from industrial units (power plants, petrochemical units, and mining activities) along with dry deposition of elements are main source of REEs in the Persian Gulf. This finding can be clearly seen in REEs map created in GIS (Fig3). The higher concentration of REEs have overlay with the location of such activities in costal shore of both provinces.

5. Conclusions

There are numerous studies about heavy metal, and other elements in the Persian Gulf. Although two ROPME cruises held in this region, but there are some unknown aspects about elements like REEs. This research carried out in order to the investigation some of REEs elements, and its relation to sediment texture, carbonate, and Tom. The result reveals that all elements have less value than average shale and upper crust. La has minimum concentration among elements (0.01 µgg-1) and Ce has the maximum level (19 µgg-1). REEs ratio La/Sc (1.6) and Ce/La ratio (2.1) were below the (UCC) and average shale (AS) ratios. Among selected elements, Ce show enrichment and other elements have EF<1. The correlation between carbonate and REEs were negatively strong which is due to the REE depletion in the marine carbonates. Some REES like La and Ce have an anthropogenic source. Except La, other elements have CVs (>30%), suggesting that their distributions might be influenced by anthological source. Spatial distribution of selected REEs in GIS approved the previous finding as well. Further investigation in REEs concentration in river flow as well as dry deposition can provide more accurate clue about actual source of REEs in the Persian Gulf.

References

Abbaslou, H., Martin, F., Abtahi, A., Moore, F., 2013. Trace element concentrations and background values in the arid soils of Hormozgan Province of southern Iran. Archives of Agronomy and Soil Science, 60:8, 1125-1143.

Agah, H., Hashtroudi, M and Baeyens, W., 2012. Trace metals and major elements in sediments of the northern Persian Gulf. Journal of the Persian Gulf, Vol3(7): 45-58.

Aide, M. T. and Aide, C., 2012. "Rare earth elements: their importance in understanding soil genesis." ISRN Soil Science , Vol(2012):1-11.

Antonina, A. N., Shazili, N., Kamaruzzaman, B., Rosnan, M, O, Y. and Sharifah, F., 2013. Geochemistry of the Rare Earth Elements (REE) distribution in Terengganu Coastal Waters: Marine Science.Vol(3).153-159.

Armstrong-Altrin, J. S. and Machain-Castillo, M. L., 2016. Mineralogy, geochemistry, and radiocarbon ages of deep sea sediments from the Gulf of Mexico. South American Earth Sciences Vol(71): 182-200.

Ashghali, F. M. and Maki, A.M., 2008. "Geochimical investigation of sediment core in the Persian Gulf coast and its biological affect", Plant and Ecosystem. Vol(12): 29-39.

Castor, S. B. and Hedrick, J. B., 2006, "Rare Earth Elements". Industrial Minerals volume, 7th edition: Society for mining, metallurgy, and exploration, Littleton, Colorado: 769-792.

Cruse, A. M., Lyons, T. W. and Kidder, D. L., 2000. Rare-earth element behavior in phosphates and organic-rich host shales: an example from the Upper Carboniferous of Midcontinent North America.Vol(66) 445-453.

Dehghan Chenari, A. and Lak, R., 2014," Effects of heavy metals from petroleum pollutions on carbonate surface sediments of the Persian Gulf". International Journal of Environmental Research.

8(2): 297-304.

Essien, J.P., Antai, N.P .and Olajire, A.A. ,2009. Distribution, seasonal variations and ecotoxicological significance of heavy metals in sediments of cross river estuary mangrove swamp. Water Air Soil Pollut . Vol197(1-4):91–105.

Kaminskas, D and Bitinas, A., 2013, "Rare earth elements of Holocene sediments in the South-Eastern Baltic Region (Nida VI borehole, Lithuania)." Geologija.Vol 55(81).1-7.

Karbassi, A. and Bayati G. R. N.B. I., 2005. "Environmental geochemistry of heavy metals in a sediment core off Bushehr, Persian Gulf." Iranian Journal of Environmental Health Science & Engineering 2(4): 255-260.

Lak, R., Mohammadi, Ali. 2013.Sedimentology of persian gulf (Comparison of Persian gulf's Sediment and Makran Sea.32ND National and 1st International Geoscience Congress.

Li, Y. H. and J. Schoonmaker, 2003, Chemical composition and mineralogy of marine sediments, in Sediments, Daigenesis, and Sedimentary Rocks (ed. F. T. Mackenzie). Elsevier-Pergamon, Oxford. Vol (7)1-35.

Liu, X., Sun,L., Li,D and Wang ,Y., 2011. "Rare earth elements in the ornithogenic sediments from the Maritime Antarctic, A potential new palaeoecology proxy." Geochemical Journal.Vol 45(1): 15-26.

López-González, N., Borrego, J., Carro, B., Grande J. A., De la Torr,M.L. and Valente, T., 2012. "Rare-earth-element fractionation patterns in estuarine sediments as a consequence of acid mine drainage: a case study in SW Spain." Boletín Geológico y Minero 123(1): 55-64.

Madhavaraju, J. and González-León, C. M., 2012. "Depositional conditions and source of rare earth elements in carbonate strata of the Aptian-Albian Mural Formation, Pitaycachi section, northeastern Sonora, Mexico". Revista Mexicana de Ciencias Geológicas 29(2): 478-491.

21

McLennan, S. M., Nance, W. and Taylor, S., 1980. Rare earth element-thorium correlations in sedimentary rocks, and the composition of the continental crust. Geochimica et Cosmochimica Acta 44 (11): 1833-1839.

Özaytekin, H. H and Uyanöz, R., 2012,"Trace and rare earth element (REE) status of Çarsamba fan soils in the ancient Konya Lake region, Turkey. African Journal of Agricultural Research. 7(7): 1110-1117.

Piper, D. Z and M. Bau .,2013. "Normalized rare earth elements in water, sediments, and wine: identifying sources and environmental redox conditions." American Journal of Analytical Chemistry. Vol(4). 69-83.

Purser, B. H(Ed)., 1973. "The Persian Gulf Holocene Carbonate Sedimentation And Diagenesis In A Shallow Epicontinental Sea spring. Speringer. p 471.

Sugden, W., 1968. Some aspects of sedimentation in the Persian Gulf. Journal of Sedimentary Research.Vol(33).355-364.

Suresh, G., Sutharsan, P., Ramasamy, V. and Venkatachalapathy, R., 2012. Assessment of spatial distribution and potential ecological risk of the heavy metals in relation to granulometric contents of Veeranam lake sediments, India. Ecotoxicology and Environmental Safety .Vol(84) 117-12.

Turekian, K. K and Wedepohl, K. H.,1961, " Distribution of the elements in some major units of the earth's crust". Geological Society of America Bulletin. 72(2)175-192.

Wang, L and Liang, T., 2015 , "Geochemical fractions of rare earth elements in soil around a mine tailing in Baotou,China". Scientific Reports. Vol(5). 1-1.

22