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Distinct depositional environments of two internal reference materials with marine sediment matrix from nearby Bangka Island

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Abstract: Internal reference materials are generated by laboratories to overcome the high cost and limited matrix of certified reference materials (CRM). Rare earth elements (REE) are strategic metals which is used in modern technology and explored within different matrices. Rare earth elements exploration surely needs appropriate reference materials for accurate interpretation. The current study aims to explain internal standard reference materials generation of marine sediment matrices from nearby the tin Bangka Island, especially the rare earth elements character, to overcome the CRM dependency. The first sample was taken with a dredger while the second one using a suction vessel. Repeated samples measurements were done by applying inductively coupled plasma - mass spectrometry (ICP-MS) from the Center for Geological Survey Indonesia for repeatability tests. The samples were analyzed in another certified laboratory in Indonesia using the same device for reproducibility assessment. The two candidates should be deposited in different environments with different influx material due to their distinct rare earth elements characters. Most of the analytes' contents are suitable to be set as internal reference material values according to acceptable repeatability and reproducibility evaluations. The internal reference materials are ready for studying suitable matrices in the future.

Keywords: Internal reference material, marine sediment, REE, repeatability, reproducibility

INTRODUCTION

Trueness and precision are important terms to draw measurement accuracy. Trueness is the degree of closeness between the mean of measurement results to a trustworthy reference value (Jochum *et al.*, 2016; Désenfant & Priel, 2017; Baydoun *et al.*, 2018) while precision is the degree of proximity between measured quantity values from replicate analysis on similar objects under specified conditions (Horstwood *et al.*, 2016; Baydoun *et al.*, 2018). Precision consists of three sections, namely repeatability, reproducibility, and intermediate precision. Repeatability is defined as precision under conditions where independent test results are done using a similar method on identical materials in the same laboratory by the same operator using the same device within short intervals of time (Hackley *et al.*, 2015; Eichbaum *et al.*, 2018). Intermediate precision is almost alike with repeatability but accomplished over an extended period of time. On the other hand, reproducibility is determined as test results from the same method on identical materials in different laboratories, operators, and device. Repeatability and reproducibility are simply evaluated by intra-laboratory and inter-laboratory comparisons, respectively (Hackley *et al.*, 2015; Yang *et al.*, 2015; Eichbaum *et al.*, 2018; Irzon & Kurnia, 2019; Miura *et al.*, 2020). It is generally complicated to gain a full degree of trueness and precision on behalf of the influence from several factors namely, observer, analytical device, calibration, environment conditions, and the time interval between analyses.

As discussed above, reference material is necessary on confirming the trueness of measurement procedures and results. Certified reference materials (CRMs) are the most trusted as they have been prepared following strict guidelines and guaranteed by proper international certifying metrology bodies like EC JRC (European Commission Joint Research Centre), NIST (National Institute of Standards and Technology, USA), BAM (Bundesanstalt für Materialforschung und –prüfung, Germany), and KRISS (Korea Research Institute of Standards and Science, Korea) to overcome difficulties in production and value assignment (Jochum *et al.*, 2016; Irzon, 2017). For geochemistry reference material in specific, a large volume of homogenous rock/sediment is needed due to intra-laboratory and inter-laboratory works. Therefore, CRMs are limited, expensive, and consist of a narrow type of matrices. This situation leads the generation of internal reference materials (also known as in-house reference materials) by laboratories globally to be used on a less frequent basis and with lower measurement costs (Christl *et al.*, 2013; Yang *et al.*, 2015; Irzon, 2017; Irzon, 2018a). In the geological sector, studies were conducted in developing such internal reference materials

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which might be improved after a proper inter-laboratories comparison and certified by a competent agency (König *et al.*, 2012; Irzon & Kurnia, 2019).

Rare earth elements (REEs) are the group of strategic metals of the lanthanides plus Yttrium (Y) and Scandium (Sc) that have similar physical and chemical properties. REE is further classified into the light-REE (LREE) which constituted of Lanthanum (La) through Europium (Eu) and heavy-REE (HREE) that consists of Gadolinium (Gd) to Lutetium (Lu) with Y and Sc. LREE is comparatively more abundant, but lower price than HREE. Rare earth metals are very important for modern devices, such as permanent magnet, catalyst, battery, radar, stealth aircraft, robotic, turbine, computer, mobile phone, and Magnetic resonance imaging (MRI) equipment. Because of the significant price and their importance for modern technology, REEs are explored in various types of rock. Granitoids, including the S-type tin-correlated intrusion, normally contain more REE than other non-altered igneous rocks. Supergene type deposits are the REE enrichment due to intensive bedrock weathering in tropical and subtropical climates (i.e. Irzon *et al.*, 2016; Yaraghi *et al.*, 2016; Ram *et al.*, 2019). The group of elements is concentrated at an economic degree within tin and bauxite tailings in various locations (Golev *et al.*, 2014; Purwadi *et al.*, 2020). Because of these reasons, tin mineralized regions are often studied for their REE composition. Various REE works were conducted in Bangka, but only the Triassic Main Range granitic rocks study from Ng *et al.* (2017) provides the complete REE with U and Th compositions.

Bangka is one of the Indonesian tin islands together with Kundur, Singkep, and Belitung. Tin mineralization in those islands is closely associated with the Southeast Asian tin belt which expands from Indonesia through Singapore, Malaysia, Burma (Myanmar), and northern Thailand (Schwartz & Surjono, 1991; Purwadi *et al.*, 2020). Tin ores were majorly exploited from the tin-bearing granite and along the river banks. Because of the lack of new primary deposit discovery, tin mining moved offshore nearby its primary source since at least two decades ago as happened in Bangka. Therefore, studies on exploring REE correlation to tin mineralization both on the land and offshore are prospective. These investigations surely need appropriate reference materials with specific matrices for analysis quality assessments. This paper aims to illustrate the generation of internal standard material with offshore sediment matrices nearby the tin Bangka Island, especially the REE composition character. The inter-laboratory analysis complements this research and evaluates the robustness of the reference value from the selected materials. On the emerging researches about REE both onshore and offshore, this material would be useful for future explorations.

GEOLOGICAL SETTING

Morphology of Bangka consists of wavy plains to hills with an altitude ranging from 0 to 699 m above sea level with Mount Menumbing at the west is the highest mountain. The Bangka capital i.e., Pangkal Pinang is situated near the east shore on the island. Geological condition of Bangka Island is drawn into two maps, namely the South Bangka Sheet (Margono *et al.*, 1995) and the North Bangka Sheet (Mangga & Djamal, 1994). The island is built of igneous, sedimentary, and metamorphic rock units from the oldest to the youngest namely, Pemali Metamorphic Complex, Tanjung Genting Formation, Klabat Granite, Ranggam Formation, and alluvium. The Carboniferous Pemali Metamorphic Complex which consists of phyllite, schist, and quartzite is the oldest rock unit in Bangka and unconformably underlies the Early Triassic Tanjung Genting Formation that constituted of alternating sandstone and claystone. More than half part of Bangka is built of Tanjung Genting Formation (Schwartz & Surjono, 1991).

Since the Late Triassic, Klabat batholith which composition range from gabbro to granite intruded both the Pemali Metamorphic Complex and Tanjung Genting Formation. Recently, Ng *et al.* (2017) subdivided Klabat batholith into several plutons based on their age with petrographic and geochemical characteristics. Most of the plutons are tin-bearing intrusions and serve as primary tin deposits. Some of the tin-associated plutons are weathered and the weathered materials turn into tin placer deposits (Purwadi *et al.*, 2020). Ranggam Formation was sedimented during Miocene to Pliocene and built of alternating sandstone, claystone and conglomerate. The Quaternary sedimentary rock units is composed of alluvium, swamp deposit, and quartz sand. The geological map of the studied Bangka island is presented in Figure 1.

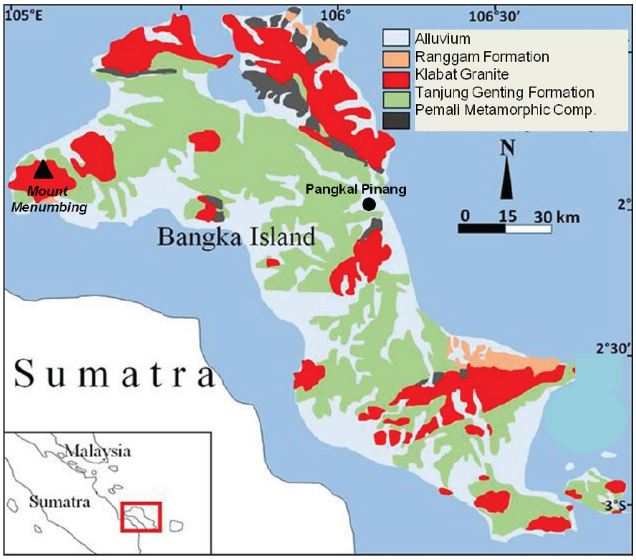

Figure 1: Regional Geology of Bangka Island which is located at the east of Sumatra (modified from Margono *et al.*, 1995 and Mangga & Djamal, 1994).

MATERIALS AND METHODS

Sample collection

Two marine sediments for internal reference material candidates in this study were taken on the work area of PT Timah Tbk which exploits tin from both land and waters at Bangka and Belitung islands. The company employs dredgers and production suction vessels for offshore works while excavators, trucks, and dozers are utilized in land minings. The first candidate (KKRK 04) is a greyish to reddish clay with a small number of quartz grains taken from a dredger of 19.5 m depth (Figure 2a). Greyish clay marine sediment from a suction vessel as shown in Figure 2c is the second sample (KHRK 11). Numbers of plastic bags were used to store the samples before they were sent to the Laboratory of Center for Geological Survey in Bandung for REE analysis.

Experimental procedures

In the laboratory, both of the samples were dried under sunlight for a day at a minimum. The samples are not hard rock, so should not be washed to prevent lost of material. Before the chemical preparation, these samples had passed through the homogeneity process. The samples were crushed, milled, and filtered to obtain the -200 mesh fraction. Internal reference material candidates were put into separated plastic barrels to be rolled manually for at least eight hours. The samples were then split and stored in glass containers (Figure 2b and 2d). Metal containers that might disturb the homogeneity during a long period of storage should be avoided. Several splits of samples were sent to another certified laboratory for reproducibility assessment.

Chloric acid ($HClO_3$), nitric acid (HNO_3), and formic acid (HOOH) and perchloric acid were added to 0.1 g of sample in Teflon glasses. The glasses were then put on a hotplate and dried until almost all of the solution evaporated. The addition of perchloric acid ($HClO_4$) is urgent if the sample is not fully destructed. Nitric acid 2% was used to dissolve the destructed material in order to keep metals in solution before the instrument analysis. AGV-2 and GBW 7113 as CRMs for this study were also prepared following the same procedure with the samples for accuracy assurance. The iCAP-Q Thermo Fisher Scientific ICP-MS setting and calibration followed the description of previous studies (Irzon & Abdullah, 2016; Irzon, 2018b). The device was chosen because of its high sensitivity and often applied in previous REE explorations and environmental studies (Kamaruzzaman *et al.*, 2011; Pradhan *et al.*, 2015; Irzon & Abdullah, 2016; Irzon, 2017; Irzon *et al.*, 2020).

Acceptance criteria

The Horwitz equation was applied to evaluate both of the intra-laboratory data and inter-laboratory data.

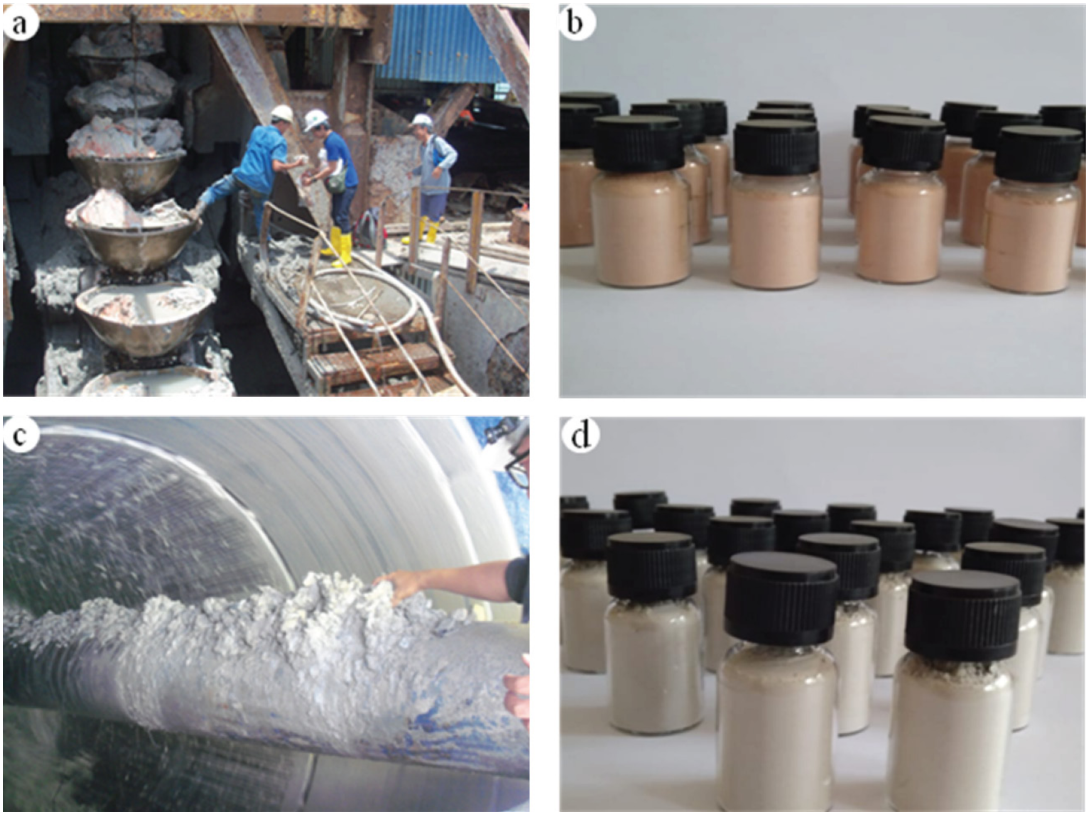

Figure 2: Field conditions and the studied samples: a) a dredger that which was used to collect KHRK 11; b) storages of the greyish to reddish clay (KHRK 11); c) KKRK 04 was attained from a suction vessel; and d) KKRK 04 in glass containers.

Four containers of the reference material candidates were randomly selected for two replicate measurements. The average value for each container analysis is expressed with Xc (Equation 1) while Wc is the absolute difference between the two analyses (Equation 2). The general mean composition of four containers (n = 4) analysis is coded Xg (Equation 3). Standard deviation from average container (S_{avc}) is determined following Equation 4 whilst standard deviation within samples (Sw) using Equation 5. S_{avc} and Sw are then used to determine the standard deviation between samples (Ss) as described in Equation 6.

$$X_c = \frac{X_{c1} + X_{c2}}{2} \qquad \text{(Eq. 1)}$$

$$W_c = |\, X_{c1} - X_{c2} \,| \qquad \text{(Eq. 2)}$$

$$X_g = \frac{\sum X_c}{n} \qquad \text{(Eq. 3)}$$

$$S_{avc} = \sqrt{(\sum X_c - X_g / n - 1)} \qquad \text{(Eq. 4)}$$

$$S_w = \sqrt{\sum X^2_g / 2n} \qquad \text{(Eq. 5)}$$

$$S_S = \sqrt{S^2_{avc} - (S^2_w / 2)} \qquad \text{(Eq. 6)}$$

Horwitz's prediction value ($\sigma = (2^{(1\text{-}0.5\log Xc)})$) and Horwitz Ratio ($H_R = Ss/\sigma$) were applied to judge the measurement results of each analytes. According to previous studies, homogeneity is established with $Ss<0.3\sigma$ and $H_R<2$ (Torres *et al.*, 2015; Sin & Wong, 2015; Samin *et al.*, 2018). Because Ss was assigned from the measurement of equal materials, procedure, and laboratory but from different containers, it informs the intra-laboratory repeatability. On the other hand, reproducibility was assessed by comparing the inter-laboratory data.

RESULTS AND DISCUSSION

Repeatability and reproducibility

The measurement results were confirmed true regarding AGV-2 and GBW 7113 analysis with the range of recovery between 82 to 120% (Table 1). According to repeatability tests, Ce, La, and Nd are the three most abundant REE in the KHRK 11 with the averages of 64.48 ppm, 45.04 ppm, and 26.67 ppm, respectively (Table 2). On the other hand, Th content in KKRK 04 is much higher than Nd with the mean of 17.74 ppm and 9.67 ppm, respectively. Both of the reference material candidates indicate almost the same Y compositions which is close to 6.30 ppm. The sample which was taken from a suction vessel is more REE+Y rich than the one from a dredger of 164.22 ppm and 103.98 ppm in comparisons.

Horwitz's prediction value of 16 elements in KHRK 11 is in the range of 1.06 to 3.60 so that the 0.3σ counted between 0.33 – 1.08. Most of the analytes standard deviation between samples (Ss) values of KHRK 11 are lower than their correlated 0.3σ to draw the sample homogeneity (Sin & Wong, 2015; Samin *et al.*, 2018; Miura *et al.*, 2020), except Ce and Nd. Nd in the sediment depicts more inhomogeneity than Ce with Ss and 0.3σ is 0.61 and 0.36, respectively (Table 3). However, the precision characteristic of the repeated measurement is acceptable due to the H_R of the analytes <2 (Wakagi *et al.*, 2017).

Table 1: CRMs measurement results for trueness assessment.

Elements	AGV 2			GBW 7113		
	Measurement result (ppm)	Certified value (ppm)	Recovery (%)	Measurement result (ppm)	Certified value (ppm)	Recovery (%)
Y	19.02	20	95.10	-	-	-
La	44.98	38	118.37	-	-	-
Ce	67.04	68	98.59	164.04	163	100.64
Pr	8.97	8.3	108.07	24.36	18.4	132.39
Nd	30.00	30	100.00	77.20	64.5	119.69
Sm	5.10	5.7	89.47	11.89	11.7	101.62
Eu	1.62	1.54	105.19	1.09	1.18	92.37
Gd	5.36	4.69	114.29	10.52	9.47	111.09
Tb	0.63	0.64	98.44	1.50	1.51	99.34
Dy	3.30	3.6	91.67	7.90	8.19	96.46
Ho	0.57	0.71	80.28	1.41	1.64	85.98
Er	1.78	1.79	99.44	4.32	4.31	100.23
Tm	0.26	0.26	100.00	0.65	0.73	89.04
Yb	1.60	1.6	100.00	4.02	4.51	89.14
Lu	0.21	0.25	84.00	0.55	0.67	82.09
Th	7.21	6.1	118.20	32.46	27.1	119.78

Table 2: Analysis results of the internal reference candidates (in ppm): a) KHRK 11; and b) KKRK 04.

a)

Analytes	Intra-laboratory data								Inter-laboratory
	Container 1		Container 2		Container 3		Container 4		
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	average
Y	6.66	6.38	6.49	6.48	6.31	5.95	6.59	6.26	6.39
La	45.06	45.04	44.34	43.92	45.89	45.52	46.13	44.45	45.04
Ce	63.97	63.77	63.71	63.58	65.43	65.38	66.24	63.81	64.49
Pr	9.14	9.06	8.90	8.64	9.20	9.14	9.33	8.87	9.04
Nd	26.70	26.53	26.58	25.71	27.06	26.93	27.81	26.07	26.67
Sm	4.84	4.78	4.74	4.66	4.83	4.82	4.89	4.67	4.78
Eu	0.05	0.06	0.05	0.05	0.06	0.05	0.05	0.06	0.05
Gd	4.58	4.43	4.35	4.27	4.44	4.41	4.46	4.27	4.40
Tb	0.35	0.34	0.32	0.33	0.35	0.33	0.34	0.32	0.34
Dy	1.58	1.53	1.42	1.48	1.55	1.52	1.60	1.50	1.52
Ho	0.19	0.18	0.16	0.17	0.18	0.18	0.19	0.17	0.18
Er	0.63	0.60	0.53	0.59	0.61	0.61	0.62	0.59	0.60
Tm	0.10	0.09	0.09	0.09	0.10	0.09	0.09	0.09	0.09
Yb	0.62	0.62	0.56	0.61	0.60	0.63	0.62	0.64	0.61
Lu	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Th	21.74	21.39	22.06	22.47	22.41	22.64	22.64	21.80	22.14
∑REE+Y	164.49	163.43	162.26	160.6	166.63	165.58	168.98	161.79	164.22

b)

Analytes	Intra-laboratory data								Inter-laboratory
	Container 1		Container 2		Container 3		Container 4		
	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	Test 1	Test 2	average
Y	6.13	5.5	6.6	6.92	5.96	5.75	6.54	6.74	6.27
La	28.47	26.53	31.06	25.01	31.89	26.29	27.7	28.77	28.22
Ce	50.13	46.03	54.36	48.19	49.35	46.38	43.66	40.66	47.35
Pr	3.82	3.38	4.37	3.62	4.45	3.46	3.73	4.06	3.86
Nd	9.81	9.35	9.55	9.22	9.89	9.72	9.49	10.28	9.66
Sm	2.29	2.13	2.59	2.23	2.54	2.17	2.25	2.48	2.34
Eu	0.33	0.33	0.34	0.33	0.33	0.31	0.32	0.3	0.32
Gd	2.53	2.35	2.75	2.44	2.72	2.38	2.41	2.53	2.51
Tb	0.19	0.18	0.22	0.18	0.2	0.18	0.18	0.2	0.19
Dy	1.27	1.22	1.36	1.23	1.27	1.19	1.19	1.24	1.25
Ho	0.18	0.18	0.2	0.18	0.18	0.17	0.17	0.18	0.18
Er	0.71	0.72	0.75	0.73	0.69	0.7	0.67	0.69	0.71
Tm	0.13	0.13	0.13	0.13	0.12	0.12	0.12	0.13	0.13
Yb	0.94	0.95	0.98	0.94	0.89	0.91	0.88	0.93	0.93
Lu	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Th	18.15	17.35	18.01	17.12	18.64	18.06	16.67	17.93	17.74
∑REE+Y	107	99.06	115.34	101.43	110.56	99.81	99.39	99.27	103.98

Even though all analytes of KKRK 04 show well precision, three of them (La, Ce, and Pr) failed to fit the intra-laboratory homogeneity criteria as the Ss values >0.3σ. Cerium is the most abundant REE with the content of 41% and 49% of ∑REE composition in KHRK 11 and KKRK 04, respectively, so that small imperfection during preparation might affect the measurement result. Moreover, cerium normally exists in Ce^{3+} state but would change to Ce^{4+} through an oxidizing environment. These candidates might have been exposed in the open air for such a long time before storage which caused some of Ce^{3+} oxidized to Ce^{4+} (Kozlova *et al.*, 2009; Ghani *et al.*, 2019) and would reduced its homogeneity.

The present reproducibility test was done by only two participating laboratories due to a limited number of ICP-MS equipped research facilities with appropriate certification in Indonesia. Two analytes (Ce and Nd) of

Table 3: Repeatability and reproducibility results of the two candidates. Grey blocks indicated unacceptable criteria.

	Repeatability						Reproducibility					
	KHRK 11			KKRK 04			KHRK 11			KKRK 04		
Analytes	Ss	0.3σ	H_R	Ss	0.3σ	H_R	Ss	0.3σ	H_R	Ss	0.3σ	H_R
Y	0.17	0.45	0.11	0.37	0.46	0.24	0.29	0.54	0.16	3.42	0.18	5.58
La	0.24	0.34	0.21	3.60	0.36	2.98	0.46	0.51	0.27	3.17	0.20	4.76
Ce	0.50	0.32	0.47	1.45	0.34	1.30	6.30	0.07	8.01	3.37	0.19	5.41
Pr	0.12	0.43	0.08	0.60	0.49	0.37	0.23	0.55	0.12	0.29	0.54	0.16
Nd	0.61	0.37	0.50	0.37	0.43	0.26	2.02	0.30	2.04	3.81	0.16	7.14
Sm	0.07	0.47	0.05	0.27	0.53	0.15	0.41	0.52	0.23	0.32	0.54	0.18
Eu	0.01	0.93	0.00	0.01	0.71	0.00	-	-	-	0.03	0.59	0.02
Gd	0.08	0.48	0.05	0.23	0.52	0.13	0.46	0.51	0.27	0.40	0.52	0.23
Tb	0.01	0.71	0.01	0.02	0.77	0.01	0.05	0.59	0.03	0.08	0.58	0.04
Dy	0.03	0.56	0.02	0.07	0.58	0.04	0.26	0.55	0.14	0.49	0.51	0.29
Ho	0.01	0.78	0.00	0.01	0.78	0.00	0.06	0.59	0.03	0.13	0.57	0.07
Er	0.02	0.65	0.01	0.02	0.63	0.01	0.06	0.59	0.03	0.34	0.53	0.19
Tm	0.00	0.86	0.00	0.00	0.82	0.00	-	-	-	0.04	0.59	0.02
Yb	0.02	0.65	0.01	0.01	0.61	0.00	0.02	0.60	0.01	0.38	0.53	0.22
Lu	0.00	1.08	0.00	0.00	0.88	0.00	0.04	0.59	0.02	0.10	0.58	0.05
Th	0.21	0.38	0.16	0.76	0.39	0.59	0.35	0.53	0.20	1.64	0.34	1.44

Tabel 4: Compositional reference values of the marine sediment internal reference materials (in ppm). Numbers in the grey blocks assigned as information values due to repeatability tests.

Analytes	KHRK 11			KKRK 04		
Y	6.52	±	0.30	7.60	±	2.28
La	44.87	±	0.79	28.41	±	2.23
Ce	66.98	±	4.26	47.89	±	4.02
Pr	9.04	±	0.21	4.10	±	0.55
Nd	27.52	±	1.53	11.18	±	0.62
Sm	4.94	±	0.28	2.50	±	0.26
Eu	0.05	±	0.01	0.34	±	0.03
Gd	4.59	±	0.33	2.70	±	0.25

Analytes	KHRK 11			KKRK 04		
Tb	0.36	±	0.04	0.22	±	0.06
Dy	1.63	±	0.18	1.45	±	0.14
Ho	0.20	±	0.04	0.23	±	0.02
Er	0.63	±	0.06	0.85	±	0.13
Tm	0.09	±	0.00	0.14	±	0.03
Yb	0.61	±	0.02	1.08	±	0.13
Lu	0.04	±	0.03	0.12	±	0.02
Th	21.98	±	0.52	18.49	±	1.39

KHRK 11 and four analytes (Y, La, Ce, and Nd) failed to meet the satisfactory reproducibility based on the standard deviation between laboratories >0.3σ and HR >2. Since only a couple of laboratories participated in this works, any slight differences would give drastic changes to the statistical characters including deviation and standard deviation. The reproducibility assessment might be improved in the future by more laboratory collaboration. However, 15 and 12 analytes concentrations of KHRK 11 and KKRK 04, respectively, are reasonable to become internal reference values according to these repeatability and reproducibility assessments.

Reference values of the candidates

Uncertainty in a set of analysis indicates an estimation of the range of inaccuracy. The uncertainty of reference values which is expressed as the standard deviations are taken into account due to possible inhomogeneity between measurements and/or within the analyzed material (Désenfant & Priel, 2017; Irzon & Kurnia, 2019). Lower uncertainty depicts a better degree of reference values. The uncertainty value for each analyte in this study is the standard deviation of the whole set of analyses. According to ISO and IAG protocols, intra-laboratory works only result in information values while reference values are set through inter-laboratory comparison. Ce-Nd and Y-La-Ce-Nd compositions of KHRK 11 and KKRK 04, respectively, are not included in the reference values because of the poor reproducibility result. However, the abundances of Y from KHRK 11 and Y-Nd of KKRK 04 are acceptable to be set as information value according to their repeatability assessments. The reference and information values of the two sediments are shown in Table 4.

Depositional environment and influx material

REE character was normalized to chondrite value (Boynton, 1984) on describing better sedimentation process (Figure 2). Ce and Eu anomalies are important on investigating alteration, weathering degree, and changing conditions of oxidation–reduction of the sedimentary zones. These indices are established using Equation 7 and Equation 8 from previous studies (Irzon & Abdullah, 2016; El-Taher *et al.*, 2019; Liu *et al.*, 2019). Ce/Ce* and Ce_N, denotes the cerium anomaly and normalized Ce composition respectively.

$$Ce / Ce^* = \sqrt{Ce_N \;/ La_N x Pr_N} \qquad \text{(Eq. 7)}$$

$$Eu / Eu^* = \sqrt{Eu_N \;/ Sm_N x Gd_N} \qquad \text{(Eq. 8)}$$

REE pattern of the two candidates is majorly identical with a sharp slope from light-REE through heavy-REE and negative Eu anomaly (Figure 3). Except for Eu and Lu of KHRK11, REEs composition of the studied samples range 1-150 fold of chondrite. However, negative Ce anomaly is shown from KHRK 11 whilst KKRK 04 with a positive one. Eu negative anomaly (Eu/Eu*) in KHRK 11 (0.04) is much deeper than the other (0.41) to suggest different influx matter and sedimentary conditions. Tropical regions are majorly warm and humid which easily leads to a strong leaching process. Therefore, the lower Eu/Eu* of KHRK 11 might be associated with a stronger leaching environment than KKRK 04 (Hu *et al.*, 2019). Moreover, the distinction could reflect the more relative abundance of detrital plagioclase feldspar with its more stable Eu^{2+} complex in KKRK 04 than the other sample (Irzon *et al.*, 2016; Irzon, 2018b; El-Taher *et al.*, 2019; Liu *et al.*, 2019; Lv *et al.*, 2020).

The redox condition of water during marine sediment deposition might be reflected from the enrichment or loss of Ce ions. Positive Ce anomaly is associated with manganese precipitation and hydrolyzation (El-Taher *et al.*, 2019; Liu *et al.*, 2019). On the other hand, Ce^{3+} is easily oxidized into Ce^{4+} in seawater leading to a negative Ce anomaly (Li *et al.*, 2020). Negative Ce anomaly is detected in KHRK 11 whilst KKRK 04 with a slightly positive one. The candidate from suction vessel might be deposited for a longer time than the one from a dredger in a more oxidized condition. Land-based rocks and shoreline erosions could also influence the degree of Ce anomaly and REE content (Ashraf *et al.*, 2016) emphasizing unequal deposition environment and influx mater of the studied samples.

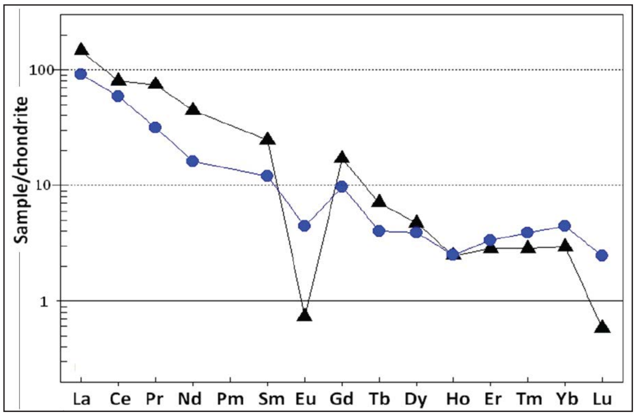

Figure 3: Chondrite (Boynton, 1984)-normalized REEs distribution pattern of internal reference candidates. Black triangle is KHRK11 while the blue circle is KKRK 04.

CONCLUSION

Intra-laboratory and inter-laboratory measurement results of two marine sediments were evaluated in generating internal reference materials. The contents of 15 and 12 analytes in KHRK 11 and KKRK 04, respectively, are acceptable to be set as internal reference values according to the high trueness and precision on reproducibility investigation. Even though poor inter-laboratory result statistics, several elements composition of the candidates are assigned as internal information values on the well intra-laboratory assessment. More laboratory collaboration might improve reproducibility evaluation. The internal reference materials are ready to be adapted in future studies of suitable matrices. The two candidates, namely KHRK 11 and KKRK 04, should be deposited in different environments with different influx material regarding their REE characters.

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AUTHOR CONTRIBUTIONS

RI designed the experiments, derived the models and analysed the data. K performed the ICP-MS measurements and helped in statistical modelling. RI wrote the manuscript in consultation with ADH, SM, and UH.

CONFLICT OF INTEREST

The authors declare that we have no conflict of interest in this paper.

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