

Thorium and Total REE Correlation in Stream Sediment Samples from Lingga Regency

Korelasi Torium dan REE Total pada Contoh Sedimen Sungai dari Kabupaten Lingga

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ABSTRACT

Rare Earth Elements (REE) are found in variety of minerals, which are mobilized by weathering from adjacent watersheds into streambeds and affect the chemical content. A study of stream sediments is useful to trace the source of metals, as they are representative of the composition of the drainage basin. This study describes trace and rare earth elements geochemistry composition of selected nine stream sediment samples from two major Islands in Lingga Regency, namely Singkep and Lingga. Moreover, the associations of rare earth elements abundance to other elements in selected samples are used on tracing the most possible mineral as REE source. Nine selected stream sediments were identified megascopically and measured for the trace and rare earth elements composition by inductively coupled plasma – mass spectrometry (ICP-MS). The selected samples from Lingga yielded very strong average Zr, Mn, Ba, and Rb compositions of 246 ppm, 172 ppm, 126 ppm, and 84 ppm, respectively. On the other hand, Zr, Mn, Cr, and Rb are the top four abundant trace elements from Singkep with consecutive median value of 486 ppm, 305 ppm, 145 ppm, and 85 ppm. Fertilizer for agricultural area at Lingga most possibly contain As and Rb upon these elements abundances and association. Tin mine activity was found to influence the streambeds composition with low Rb-Cs composition but high Zr-REE abundance. Very strong Th to Σ REE association suggests that thorium-bearing mineral, especially monazite-La, is the main REE source of the selected samples. All of the studied samples exhibit Eu negative anomaly to imply the absence of either detrital apatite or chemical weathering of apatite. Moreover, REE of Lingga stream sediments is averagely more fractionated than Singkep.

Keywords: stream sediments, Lingga Regency, monazite, REE

ABSTRAK

Unsur Tanah Jarang (UTJ) terkandung dalam berbagai jenis mineral yang dapat termobilisasi akibat pelapukan dari daerah aliran sungai terdekat, terendapkan, dan mempengaruhi kandungan kimianya. Studi mengenai sedimen sungai dapat dimanfaatkan untuk menelusuri sumber logam, sebagaimana sedimen tersebut merupakan bahan penyusun dasar sungai. Penelitian ini menerangkan kandungan geokimia unsur jejak dan tanah jarang dari sembilan contoh sedimen sungai terpilih dari dua pulau besar di Kabupaten Lingga, yaitu: Singkep dan Lingga. Selanjutnya, asosiasi kelimpahan unsur tanah jarang terhadap unsur lain dipergunakan untuk menelusuri mineral yang paling mungkin sebagai sumber UTJ. Sembilan contoh sedimen sungai terpilih telah dideskripsi secara megaskopis dan diukur kandungan unsur jejak dan tanah jarangnya menggunakan inductively coupled plasma – mass spectrometry (ICP-MS). Contoh terpilih dari Pulau Lingga tersusun atas sejumlah tinggi Zr, Mn, Ba, dan Rb, yaitu 246 ppm, 172 ppm, 126 ppm, and 84 ppm secara berurutan. Sementara itu, Zr, Mn, Cr, dan Rb merupakan unsur paling melimpah pada contoh dari Pulau Singkep dengan rata-rata kelimpahan masing-masing 486 ppm, 305 ppm, 145 ppm, and 85 ppm. Pupuk pertanian di Lingga kemungkinan

besar mengandung As dan Rb berdasarkan kelimpahan dan asosiasi mineral tersebut. Aktivitas penambangan timah ditengarai mempengaruhi komposisi endapan sungai dengan komposisi Rb-Cs yang rendah tetapi Zr-REE melimpah. Korelasi kuat Th dan Σ UTJ menunjukkan bahwa mineral mengandung thorium, khususnya monasit-La, merupakan sumber utama UTJ pada contoh terpilih. Seluruh contoh menampakkan anomali negatif Eu yang menandakan ketiadaan apatit detrital maupun pelapukan kimia apatit. Lebih jauh, UTJ pada sedimen sungai Lingga secara rata-rata lebih terfraksinasi dari pada Singkep

Kata kunci: sedimen sungai, Kabupaten Lingga, monasit, UTJ.

INTRODUCTION

Background

Soils, sediments, and rocks from the drainage basin upstream of the collection site build the stream sediment. Instead of be considered as a sink for trace metals, stream sediments can act as source of metals depending on the change of the environmental condition [1–5]. The contaminations sources can be estimated from stream sediment analysis, which usually not detected on water monitoring [1]. The catchment size, catchment geology, variable relief, pH and Eh of the stream water, and exposed mineralization are factors that affect the drainage geochemistry. The use of stream sediment geochemical survey in the search for mineral deposits is based on the premise; those sediments contain elements that are mobilized by weathering from adjacent watersheds into streambeds. Consequently, the chemistry of the sediments is a representative of the drainage basin composition [5,6].

Sumatera Island and its surrounding are composed of three groups of granite, namely Main Range Province, Eastern Province, and Volcanic Arc Belt. The-S type granite in Lingga Regency is a part of the Main Range Province, which is widely distributed as isolated plutons and batholiths over the whole island. The Eastern Province is composed of I-type granites that spread from the eastern Malaysia to Bintan Island. The youngest group is Volcanic Arc Belt that form small

batholiths which are confined to the Barisan Range [7]. Lingga Regency is located in Riau Islands Province with Daik as the capital. Tin was produced massively in Lingga Regency for more than four decades and was one of the three main resource locations in Indonesia besides Bangka and Belitung [8,9]. The tin exploitation was centered in Dabo, Singkep Island. The study location is situated in Sundaland on the southeast margin of Eurasia. The tin resource is considered to be correlated with the granite in studied location as it is located in the Main Range Granite Province of South East Asia [7,8,10–13]. Previous investigations confirm that monazites are detected both in S-type granite [14–16] and in A-type granite [17–19]. No previous study reported on monazite occurrence in I-type granite. Alor, Daik, Petengah, Panggak, Musai, Semarung, Setajam, Jelutung are some rivers in Lingga Island whilst Cikasim, Buluh, Serak, Langkap, Langkap, and Manggu are situated in Singkep Island. These rivers are actually containing elements that represent the adjacent watersheds so they are useful to be investigated.

Rare Earth Elements (REE) are a set of fifteen chemical elements in lanthanide group. Despite their name, REE are relatively plentiful, as cerium (Ce) comprises more of the Earth's crust than copper (Cu) and lead (Pb) [20]. Although REE comprise significant amounts of many minerals, almost all production came from less than 10 minerals,

such as apatite, bastnasite, monazite, xenotime, gadolinite, and cerianite. Those minerals are described with different elemental formulas, which are mobilized by weathering from adjacent watersheds into streambeds and affect the chemical content.

No previous study been conducted to define geochemistry composition of stream sediments in Lingga Regency. The aim of this study is to describe trace and rare earth elements geochemistry composition of nine selected stream sediment samples from two major islands in Lingga Regency, namely, Singkep and Lingga. These stream sediment compositions are then tried to be correlated geochemically to rock units in the regency. Several minerals are described as source of REE. In this research, the association of Th-REE abundance in selected samples is used to trace the most possible mineral as the source of REE.

Geological Setting

Lingga Regency consists of 531 islands with Singkep and Lingga as the two major islands. The general geology of this region consists of a pair of metamorphic rocks units, a couple of intrusive rock units, four sedimentary rock formations, and a pair of surficial deposits [21]. The Bukitduabelas Quartzite and Persing Metamorphic Complex are the two oldest rock units, which emplaced in Carboniferous. Previous study reported that the Persing Metamorphic Complex in both Singkep and Selayar Islands intruded by Late Triassic Muncung Granite and Jurassic Tanjungbuku Granite. However, Muncung Granit was also detected in Lingga island during field work and strengthened by geochemistry interpretation [8,22]. Muncung Granite was classified as S-type whilst Tanjungbuku as I-type [23].

The Tanjungdatuk Formation deposited in Jurassic period and dominated by low grade metamorphic, foliated, sedimentary rock units comprising metasandstone, metaclaystone, and metasilstone alternating with grey to reddish brown chert. This formation is unconformably overlain by three types of other local sedimentary units, from the oldest to the youngest, namely the Tengkis Formation, the Pancur Formation, and the Semarung Formation. Tengkis Formation is dominated by quartz sandstone with grey shale intercalation whilst Pancur Formation consists of altered red shale and red sandstone. The Semarung Formation with its type locality situated in Semarung River, Lingga, are presumed to be of Cretaceous age. The youngest rock units are the pair of Quaternary deposits comprising the Alluvium and the Swamp Deposit [21]. The geological map of Lingga Regency is shown in Figure 1.

ANALYTICAL METHOD

Sampling and Description

Nine stream sediments were collected from different locations in Lingga Regency, six samples were attained at Lingga Island whilst three others on Singkep Island. Various types of rock float such metasediment, granitoid, and conglomerate were indicated in Setajam River. Sample code SSL 32 was a stream sediment sample from Setajam River (Figure 2a) in Lingga Island which is composed of clay grains, fine to rough sand, and gravels. Less heavy metals were detected megascopically in SSL 77 (Figure 2b) which was taken from Daik River, Lubuk Papan. The SSL 81 is another sample from Daik flows, mostly constructed of dark fine sand and less amount of clay than SSL 77. Alor is another river in Lingga, which also flows through Resun Village where SSL 78 was attained as yellowish-

brownish sandy stream sediment sample. Resun Waterfall is located in North Lingga District with more than 100 m height and slope of about 45°. Sample near the Resun Waterfall was a fine and light grain sand with minor composition of clay (SSL 79) as it was grabbed in swift flowing Resun River (Figure 2c and 2d). Granitoid float was found in Kelumu River, which is located about 1 km before the southwest coast of Lingga (Figure 2e). Stream sediment from Kelume (SSL 80) is composed mostly by medium grain sand with some dark minerals.

Three samples were obtained from Singkep Island, southwest of Lingga Island. Balerang Water Spring is a famous tourist location in Singkep Island near SSS 48 and

SSS 50 samples attained. The SSS 48 is located near the waterfall about half kilometer from Balerang Water Spring whilst SSS 50 is situated after abandoned tin mine (Figure 2f) approximately 1 km from SSS 48. The SSS 48 is relatively built of coarse quartz grain and less mafic fraction than SSS 50. The SSS 72 is constructed mostly of quartz sand and minimum mafic grain which was taken near to the mouth of the river in Kebun Nyiur (Figure 2g and 2h). This last sampling point is also located just after local tin tailing and approximately 200 m before southeast coast of Singkep. Resume of the nine studied stream sediments from Lingga Regency is displayed in Table 1.

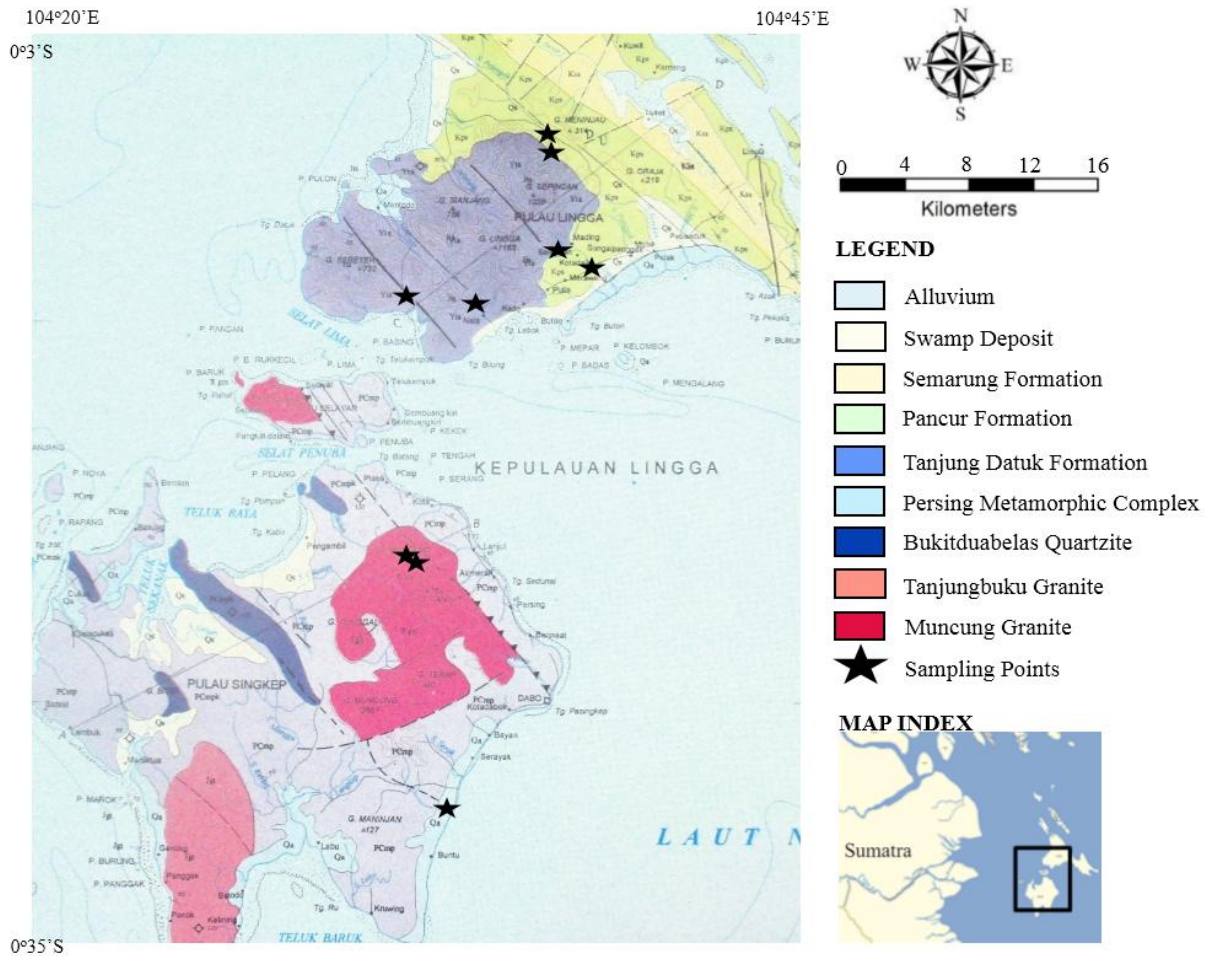


Figure 1. Geological Map of Study area and sampling points [21].

Table 1. Summary of stream sediment samples from Lingga Island and Singkep Island, Lingga Regency

Location	Sample Name	Megascopic Stream sediment Description
Kelume, Lingga	SSL 32	clay grain, fine to rough sand, and gravels
Lubuk Papan, Lingga	SSL 77	mix of sandy and clayish fraction with minimum heavy metals indication
Resun, Lingga	SSL 78	yellowish to brownish sand
Panggak Darat, Lingga	SSL 79	fine and light grain sand with minor composition of clay
Kelume, Lingga	SSL 80	medium grain sand with some dark minerals
Merawang, Lingga	SSL 81	dark fine sand and low amount of clay
Sungai Harapan, Singkep	SSS 48	coarse quartz grain and low mafic fraction
Sungai Harapan, Singkep	SSS 50	coarse quartz grain and medium mafic fraction
Batu berdaun, Singkep	SSS 72	quartz sand and minimum mafic grain near the mouth of the river in Kebun Nyiur



Figure 2. Field conditions in Lingga Regency: a) Setajam River of SSL 32; b) more clay composition of SSL 78 than SSL 79 (c) although the two samples were attained from Resun's flow; d) swift flow of Resun river at the location of SSL 79; e) a part of Daik River in the location of SSL 81; f) tin mining clearly affect the water colour of SSS 50's site as also was noticed in SSS 72 (g); and h) SSS 72 majorly consists of quartz sand with minimum mafic fraction.

Sample Analysis

In the laboratory, the collected stream sediment samples were dried in sun heat for minimum one day. Whole samples were then crushed with jaw crusher and ball mill to obtain particle size of ~200 mesh. This particle size was selected to optimize acids destruction on the next preparation procedure. Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) instrument in the Center for Geological Survey of Indonesia is the only geochemistry instrument of this investigation that focused on trace and rare earth elements analysis. Samples were dissolved with three acid leaching using nitric acid (ultra pure grade), formic acid (ultra pure grade), and perchloric acid (pro analysis grade). The CPS (counts per second) of one blank and six levels of calibration solutions (0.1, 1, 5, 10, 25, and 50) measured to obtain the calibration curves of the analyzed elements. Computer program of the ICP-MS device transformed CPS elements of samples to concentrations using the previous calibration curves. The andesite AGV-2 and rhyolite GBW 7113 were two certified reference materials (CRMs) used in this study to certify the quality of measurement results. All the CRMs and the samples were analyzed in three repetitions to ensure the good quality of measurements. Total of twenty trace elements (Li, Be, Sc, V, Cr, Mn, Ga, As, Rb, Sr, Y, Zr, Nb, Cs, Ba, Tl, Pb, Bi, Th, U) plus the rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were analyzed.

RESULT AND DISCUSSION

Measurement Accuracy

The accuracy of preparation and measurement procedures were verified using two CRMs, andesite AGV-2 and rhyolite GBW 7113. All studied samples and CRMs

were measured three times to establish the measurements stability on their relative standard deviations (RSD). The applied ICP-MS in this study was relatively stable with RSD <5% for most analyzed elements, except As (12%), Nb (7%), and Pb (6%). Although Tm recovery is only 78%, the measurement results are reliable on good recovery ranging from 80% - 120%. The comparison of analysis results and standard values for CRMs are shown in Table 2.

Trace Elements Composition

The trace and rare earth elements compositions of the selected six stream sediment samples from Lingga Island (SSL 32, SSL 77, SSL 78, SSL79, SSL 80, and SSL 81) together with three others from Singkep Island (SSS 48, SSS 50, and SSS 72) are listed in Table 3. The selected samples from Lingga yielded very strong Zr, Mn, Ba, and Rb with mean values of 246 ppm, 172 ppm, 127 ppm, and 84 ppm respectively. On the other hand, Zr, Mn, Cr, and Rb are the top four abundant trace elements from Singkep with the average values of 486 ppm, 203 ppm, 145 ppm, and 85 ppm respectively. The comparisons of mean elemental values of the two islands are then simplified in histogram (Figure 3). Elements, such Ba, Ba, Be, Sc, Ga, As, Y, Th, and Σ REE, are more concentrated in Lingga whilst higher Cr, Mn, Zr, Nb, Sr, Tl, Bi, and U contents are observed in Singkep stream sediments. Mean concentration values of Rb, Cs, and V in selected sediments form Lingga and Singkep are relatively equal of 84 and 85 ppm, 6.70 and 7.10 ppm, and 23.67 and 25.77 ppm respectively. The REE content of studied stream sediment samples is ranging from 11 ppm (SSS 72) to 537 ppm (SSL 80). Cerium, Lanthanum, and Neodymium have considerably high concentrations when

compared with other rare earth elements. The interrelation between elements determined during a geochemical survey in Lingga quantified by the use of correlation coefficients (r). On the other hand, interelemental associations of samples from

Singkep are not evaluated because it is only distributed in three data. Good correlations in this study are based on $r \geq 0.75$ whilst lower values as such values indicate very weak associations between elements as presented in Table 4.

Table 2. Results of analysis on certified reference materials (CRM) in comparison with certified values (ppm). The accuracy, calculated from the relative error of the certified values of the CRMs was $<20\%$.

	AGV-2				GBW 7113			
	Mean Value	RSD (%)	Certified Value	Recovery (%)	Mean Value	RSD (%)	Certified Value	Recovery (%)
Trace Elements (ppm)								
Li	-	-	-	-	15.79	1.04	17.5	90.23
Be	1.94	2.11	2.3	84.13	-	-	-	-
Sc	10.61	0.09	13	81.62	-	-	-	-
V	102.30	0.03	120	85.25	57.01	0.08	64.3	88.66
Cr	14.98	0.46	17	88.12	-	-	-	-
Mn	637.60	0.51	770	82.81	-	-	-	-
As	-	-	-	-	4.81	11.98	5.96	81.28
Rb	59.39	0.32	68.8	86.32	154.50	0.69	183	84.43
Sr	534.70	0.44	658	81.26	-	-	-	-
Y	16.35	0.09	20	81.75	22.51	1.09	28	80.39
Zr	233.40	2.46	230	101.48	271.70	4.43	335	81.10
Nb	13.13	7.16	15	87.53	-	-	-	-
Cs	-	-	-	-	6.36	0.98	7.16	88.78
Ba	931.60	0.04	1140	81.72	-	-	-	-
Tl	33.26	0.17	38	87.53	-	-	-	-
Pb	61.95	5.91	68	91.10	-	-	-	-
Bi	7.10	0.50	8.3	85.52	10.73	1.01	13.2	81.29
Th	26.27	0.32	30	87.57	38.25	0.88	47.2	81.04
U	-	-	-	-	6.98	0.72	8.63	80.88
Rare Earth Elements (ppm)								
La	-	-	-	-	1.86	0.64	1.96	95.00
Ce	-	-	-	-	6.25	1.16	6.54	95.50
Pr	-	-	-	-	0.88	2.11	0.99	88.38
Nd	3.37	1.468	3.6	93.58	4.75	1.68	5.32	89.19
Sm	-	-	-	-	0.97	2.51	1.1	88.55
Eu	-	-	-	-	2.76	0.77	2.93	94.13
Gd	-	-	-	-	0.42	1.10	0.5	84.60
Tb	-	-	-	-	2.53	1.26	3.15	80.38
Dy	-	-	-	-	0.43	1.73	0.49	87.96
Ho	-	-	-	-	0.86	2.45	1.02	84.31
Er	14.86	0.611	13	114.31	100.50	1.01	97.7	102.87
Tm	-	-	-	-	0.07	3.81	0.09	77.78
Yb	6.53	1.545	6.1	106.98	14.60	0.93	16.7	87.43
Lu	1.91	0.3	1.88	101.49	2.90	1.47	3.04	95.33

Thorium and Total REE Correlation in Stream Sediment Samples from Lingga Regency
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Table 3. Trace and rare earth elements compositions of selected nine stream sediment samples from Lingga Regency.

	From Lingga Island												From Singkep Island					
	SSL 32	RSD (%)	SSL 77	RSD (%)	SSL 78	RSD (%)	SSL 79	RSD (%)	SSL 80	RSD (%)	SSL 81	RSD (%)	SSS 48	RSD (%)	SSS 50	RSD (%)	SSS 72	RSD (%)
Trace Elements (ppm)																		
Li	18.56	0.87	23.46	1.16	8.67	0.38	22.86	0.47	53.12	1.03	19.42	0.99	45.59	0.77	36.52	0.25	12.33	0.15
Be	1.79	2.30	2.05	0.60	1.70	0.03	2.00	0.50	1.09	1.93	1.52	3.09	1.50	1.55	0.71	5.72	0.49	3.42
Sc	8.94	1.12	6.32	2.42	3.40	0.03	6.28	0.40	3.71	1.36	5.38	0.28	2.54	0.16	3.06	2.24	0.44	0.28
V	37.11	0.71	15.09	1.37	37.82	0.11	14.97	0.82	15.42	0.80	21.58	1.25	33.15	0.86	19.94	1.80	24.23	0.58
Cr	47.44	0.24	29.25	1.11	174.79	0.17	11.84	7.61	23.61	1.95	135.96	8.26	177.03	0.66	56.71	6.99	202.18	0.77
Mn	290.00	0.25	210.45	0.79	124.56	0.70	218.25	0.67	112.08	0.74	79.77	14.42	376.70	1.40	233.40	0.62	<0.01	0.57
Ga	9.58	0.29	10.33	0.39	9.02	0.15	10.20	0.64	4.44	0.86	7.56	0.68	5.93	0.60	2.77	1.45	0.86	0.54
As	11.52	1.01	30.93	5.28	7.46	0.35	16.58	21.65	<0.01	7.31	5.00	19.14	1.89	16.08	<0.01	25.40	<0.01	2.01
Rb	88.66	0.19	116.60	0.48	74.65	0.17	114.40	0.43	30.21	0.30	80.17	0.42	187.43	0.48	62.14	1.47	7.84	0.25
Sr	10.21	0.47	5.88	0.56	31.36	0.06	5.35	0.44	2.30	1.37	7.44	0.31	18.85	0.86	8.52	0.32	74.99	0.91
Y	17.87	1.01	25.88	0.12	28.00	0.14	27.43	0.61	35.64	0.33	16.90	0.58	28.17	1.24	25.87	1.63	1.96	1.47
Zr	239.16	0.66	307.86	0.65	173.88	0.32	148.54	0.35	431.76	1.44	178.22	0.60	519.24	1.49	876.12	0.83	64.62	1.58
Nb	15.96	1.37	30.51	0.78	29.42	0.46	21.35	1.48	10.84	2.48	17.94	2.02	7.95	0.98	11.06	3.58	183.00	1.16
Cs	5.86	0.45	7.88	0.28	8.31	0.02	7.93	0.42	4.70	0.30	5.40	0.79	14.49	0.79	5.88	0.86	0.84	0.68
Ba	194.80	0.71	141.72	0.54	163.92	0.29	137.28	0.26	9.05	0.80	114.68	0.31	119.30	1.25	41.31	1.43	12.88	0.46
Tl	0.77	4.38	0.29	2.51	0.31	0.01	0.35	0.44	<0.01	2.88	<0.01	14.27	1.46	11.18	5.82	10.13	<0.01	2.49
Pb	22.75	0.89	28.63	0.29	103.80	0.19	29.61	0.27	20.05	0.39	15.97	0.15	26.30	1.03	22.85	0.41	9.21	0.51
Bi	1.69	2.32	<0.01	13.33	<0.01	0.02	<0.01	34.16	3.00	3.48	<0.01	4.22	1.75	6.04	2.63	0.98	<0.01	3.98
Th	15.22	1.88	23.27	0.73	12.84	0.07	22.38	0.49	75.22	0.81	14.82	0.56	17.53	0.48	37.66	0.76	2.80	0.33
U	4.96	0.46	4.94	0.44	4.69	0.03	4.95	0.66	19.37	0.57	3.60	0.85	12.90	2.77	20.53	2.12	0.91	1.20
Rare Earth Elements (ppm)																		
La	19.51	0.50	28.90	0.37	38.94	0.11	29.63	2.31	103.20	0.89	17.87	0.56	17.96	1.30	42.78	0.40	1.83	0.56
Ce	37.35	0.73	76.52	0.47	60.01	0.34	83.45	3.31	248.88	0.56	42.68	0.59	34.41	6.23	89.61	0.47	5.51	0.13
Pr	4.46	0.59	6.23	0.70	6.66	0.02	6.42	3.52	28.57	0.61	3.79	0.34	4.56	0.90	10.90	1.29	0.35	0.32
Nd	16.95	0.88	23.10	0.35	23.36	0.19	23.94	4.30	99.44	0.69	14.16	0.89	17.06	1.25	39.93	0.34	1.27	0.78
Sm	3.48	0.84	5.35	0.90	5.28	0.04	5.36	6.03	21.24	0.20	3.25	0.24	3.90	0.54	8.14	1.91	0.29	1.27
Eu	0.46	1.28	0.53	0.41	0.53	0.00	0.53	0.97	0.10	1.81	0.36	2.62	0.14	1.90	0.08	4.59	0.04	2.65
Gd	3.84	1.24	4.46	1.47	4.47	0.02	4.52	2.79	12.62	0.72	2.70	2.10	3.80	3.79	6.61	3.25	0.28	1.10
Tb	0.56	4.25	0.83	0.54	0.94	0.01	0.85	1.19	1.73	1.28	0.52	1.02	0.67	1.78	0.89	7.39	0.06	1.37
Dy	3.77	3.30	5.27	0.59	6.10	0.04	5.32	2.02	7.65	0.28	3.28	0.63	4.94	4.20	5.07	12.09	0.40	3.45
Ho	0.87	1.34	1.25	1.01	1.36	0.02	1.25	0.44	1.57	0.82	0.78	2.76	1.07	1.78	1.10	5.69	0.11	8.47
Er	2.55	3.42	3.45	0.68	3.48	0.02	3.41	1.30	4.25	1.81	2.19	0.81	3.47	0.30	3.78	4.53	0.28	12.62
Tm	0.43	4.53	0.60	2.47	0.57	0.01	0.61	1.52	0.80	0.27	0.40	3.05	0.63	2.01	0.68	15.07	0.06	5.26
Yb	2.90	10.46	4.21	0.44	3.59	0.01	4.10	0.64	5.97	0.38	2.69	1.39	4.97	0.16	5.50	4.70	0.40	0.64
Lu	0.45	3.25	0.65	0.35	0.52	0.00	0.67	1.22	1.11	0.97	0.43	2.80	0.79	2.60	0.97	1.54	0.08	1.68
ΣREE	97.57		161.35		155.80		170.06		537.14		95.10		98.37		216.03		10.96	

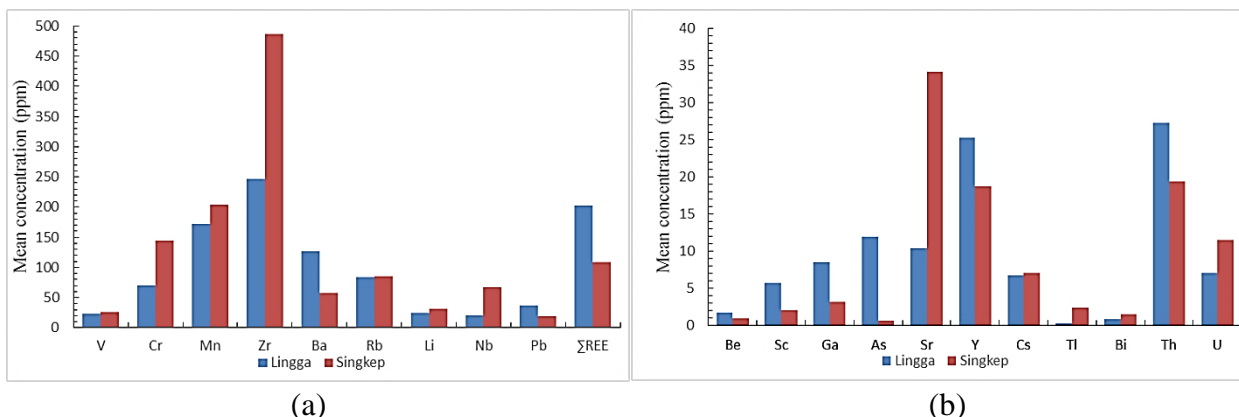


Figure 3. Histograms of mean elements abundance of Lingga and Singkep stream sediments: a) high concentrations elements; and b) low concentrations elements.

Table 4. Correlation matrix between elements of the Lingga stream sediments. Green boxes indicate good elements associations whilst uncolored boxes represent very weak correlations.

	Mn	Ga	As	Rb	Sr	Y	Zr	Nb	Cs	Ba	Tl	Pb	Th	U	ΣREE
Li	-0.2180	-0.7760	0.6180	-0.6226	-0.6708	0.6374	0.8579	-0.6677	-0.6398	-0.9018	0.0316	-0.5317	0.9724	0.9354	0.9208
Be	0.6461	0.9841	0.8846	0.9753	0.1208	-0.3755	-0.5757	0.7082	0.7894	0.7834	-0.3652	0.1252	-0.7334	-0.7913	-0.7400
Sc	0.8535	0.5646	0.2615	0.5702	-0.3496	-0.6557	-0.2035	-0.1060	-0.0367	0.6005	0.8027	-0.5013	-0.4238	-0.4452	-0.5363
V	0.1984	0.2193	-0.5905	-0.0933	0.7745	-0.3983	-0.3708	0.1342	0.1167	0.6331	0.5412	0.5886	-0.5028	-0.3606	-0.4333
Cr	-0.5607	-0.0220	-0.7073	-0.1806	0.7963	-0.3080	-0.4759	0.3267	0.1426	0.2680	-0.1913	0.6645	-0.4739	-0.3860	-0.3806
Mn		0.6510	0.4689	0.5723	-0.1576	-0.2605	-0.1025	0.0901	0.2713	0.6083	0.7914	-0.1928	-0.2982	-0.3039	-0.3508
Ga			0.7891	0.9417	0.2501	-0.4595	-0.6556	0.7054	0.7840	0.8792	-0.2132	0.2163	-0.8207	-0.8534	-0.8164
As				0.8716	-0.4482	0.4281	0.7377	0.5281	0.4698	-0.0465	-0.3704	-0.2551	0.8680	0.5886	0.5660
Rb					-0.0304	-0.4517	-0.5908	0.6345	0.6944	0.7091	-0.3100	-0.0373	-0.7238	-0.8055	-0.7559
Sr						-0.0389	-0.4581	0.5471	0.5196	0.4844	-0.1805	0.9545	-0.4823	-0.3709	-0.3398
Y							0.5788	-0.0479	0.0776	-0.6674	-0.9673	0.2295	0.7644	0.7561	0.8425
Zr								-0.4088	-0.5308	-0.7092	0.1242	-0.3498	0.8665	0.8573	0.8267
Nb									0.9005	0.5409	-0.8571	0.6134	-0.5953	-0.6193	-0.5168
Cs										0.5780	-0.9819	0.6315	-0.5620	-0.5845	-0.4691
Ba											0.8782	0.3359	-0.9145	-0.8782	-0.8997
Tl												-0.4194	-0.4007	0.3957	-0.9670
Pb													-0.3212	-0.2301	-0.7033
Th														0.9873	0.9858
U															0.9868

Trace elements such as Cr, Co, Ni, Cu, Zn, As, Cd and Pb are not presenting any biological function and they are particularly toxic and harmful for living organisms. These elements, also called “Potential Harmful Elements” which might originate from natural processes (rock weathering, volcanic eruption) and also from various anthropogenic activities (mining, industrial

emissions, domestic effluents and agriculture [1,24]. High As content varying up to 30 ppm in samples collected in Lingga while in Singkep is below 2 ppm. These As positive anomalies are usually associated with sulphide mineralization and anthropogenic activities. Many rice fields and plantations are located in Lingga [25]. Due to the absence of sulphide mineralization in Lingga, these As

positive anomalies are possibly associated with the application of fertilizers and As-rich agricultural chemicals [1] which are possibly widely used in Lingga cultivated land. Moreover, potassium rich fertilizers may also cause Rb anomaly as detected in southwest Hungary [26]. Strong As-Rb association is revealed with $r = 0.87$ to inform that fertilizers for agricultural area at Lingga most possibly contain As and Rb.

Lithium is a lithophile metallic element, occurring predominantly in silicate minerals, and widely present as an accessory element in K-feldspar, biotite mica, amphibole and clay minerals where it can substitute for K, Na and Mg. K-feldspar and biotite were detected in Muncung Granites samples at the range of 29-50% and up to 7% respectively [8]. SSL 80, SSS 48, and SSS 50 were sampled in the area of Muncung Granite to explain their high Li contents. Elevated REE values are generally indicative of felsic rocks, especially intrusives, and the soil and stream sediment derived from them. Silicate minerals are more concentrated in felsic rock to confirm very strong correlative coefficient of Li against total REE of 0.92 (Table 4).

The mean vanadium (V) concentration in the stream sediments from Lingga is almost equal to Singkep. No other trace and/or rare earth elements show good interrelation to V. In addition, scattered V stream sediment point anomalies on studied location might be caused by local geological substrate or by coprecipitation conditions in that should be investigated locally. Chromium is a lithophile metallic element and its elevated Cr value is an indicative of mafic or ultramafic rocks [3], [27]. Very low Cr contents in association with elevated values of K, Th, U and REE may indicate the presence of felsic rocks, which explain the chemical abundances on SSS 48-SSS 50. The two samples are located on

Muncung Granite domain in which the decrease of Cr is parallel to Th, U, and REE elevations. Only Sr that was indicated to have good association to Cr in Lingga stream sediments ($r = 0.80$). Manganese is also typically enriched in mafic and ultramafic rocks relative to felsic lithologies. Although SSS 48 was located in granitoid domain, several mafic minerals were detected in the sample megascopically which most probably increase the Mn abundance. Mn associated well to Tl and Sc with correlative coefficient values of 0.79 and 0.85 respectively (Table 4).

Rubidium is a member of the alkali metal that does not form any minerals of its own, but is present in several common minerals in which it substitutes for potassium. The Rb⁺ ion substitutes for K⁺ in mica such as muscovite and in K-feldspar such as microcline and orthoclase. It is also associated with greisen-type Sn deposits and is found enriched in most ore zones of porphyry-copper deposits [26]. Tin mining started in Lingga Regency, especially in Singkep island, since four decades ago [28]. Wedephol (in [3]) proposed that Cs which is more concentrated in more differentiated rock. Granitoids are relatively more differentiated than mafic and intermediate rocks. Those evidences confirm Rb-Cs high anomaly in SSS 48, which was taken at Muncung Granite area. SSS 50 was actually located on Muncung Granite domain but was taken just after abandoned tin mine which decrease Rb-Cs but massively increase Zr-REE abundances on comparison to SSS 48.

Beryllium was proposed to be more concentrated in evolved granite [26]. Its concentration in SSS 48 (1.5 ppm) is lower than continental crust value (1.7 ppm, [29]). Muncung Granite was suggested to be consist of two facies, namely, A facies from Singkep

and B facies from Lingga and Selayar [8]. The low Be concentration together with very strong and good correlation are shown on Rb-Be (0.97) and Cs-Be (0.79) respectively might inform that A facies of Muncung Granite is not classified as a highly evolved granite. Comparison on SiO₂ range in the two facies (71.25 – 72.71 % in A facies and 71.34 – 76.16% in B facies,[8]) is parallel with this fact.

SSS 72 is an anomalous sample in this study. The lowest Be, Sc, Mn, Ga, As, Rb, Y, Zr, Cs, Tl, Bi, Th, and U contents are indicated on this sample. On the other hand, SSS 72 is most concentrated in Cr, Sr, and Nb. The sample was attained just near the mouth of the Langkap River in Kebun Nyiur and is constructed mostly of quartz sand and minimum mafic grain. Ba/Sr ratio is decreasing along magmatic evolution. Metamorphic rocks were formed by heat, pressure, and chemical processes, usually while buried deep below Earth's surface. Persing is a metamorphic complex and is the oldest unit in the study area (together with Bukitduabelas Quartzite) which is formed on Carboniferous era. Langkap River flows through Persing Metamorphic Complex to match the minimum Ba/Sr (0.17, Tabel 1) ratio in SSS 72 relative to other samples. More detail research should be conducted about high Nb composition in Persing Metamorphic Complex, as this element is far more abundant in SSS 72 than other samples.

REE and Th Correlation in the Stream Sediments

The rare earth elements (REEs) are the elements from lanthanum to lutetium (atomic numbers 57–71) in the periodic table. La, Ce, Pr, Nd, Sm and Eu being described as light rare earth elements (LREE) whilst Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu as heavy rare earth

elements (HREE). Typically, the light REE (La to Sm) reside in minerals such as apatite, epidote, allanite, sphene and monazite whereas the heavy REE (Gd to Lu) are associated with minerals such as zircon, garnet and xenotime [29–31]. Due to their chemical similarity, the concentrations of rare earths in rocks are only slowly changed by geochemical processes, making their proportions useful for geochronology and dating fossils [32]. The good Zr- Σ REE correlation (0.83) is indicative of zircon in the selected samples. Nevertheless, zircon is not the major source of REE in Lingga as lower Zr-HREE (0.7) than Zr-LREE (0.82) association because this mineral should be more correlated to HREE.

Yttrium is chemically similar to the lanthanides and it has often been classified as a part of rare earth element [28]. ⁸⁹Y is the only naturally occurring isotope of the elements which is strongly partitioned into garnet, hornblende, clinopyroxene and biotite. Yttrium shows slight enrichment in granitic (ca. 40 mg kg⁻¹) relative to intermediate (ca. 35 mg kg⁻¹) and basaltic (ca. 32 mg kg⁻¹) igneous rocks [26] to explain that elevated Y and REE values are generally indicative of felsic rocks, especially intrusives, and the soil and stream sediments derived from them. In specific, the electron configuration and ionic radius of Y resemble those of the heavier REEs (Gd to Lu) to describe the much stronger relative coefficient of Y-HREE (0.99) than Y-LREE (0.84) and Y- Σ REE (0.84) (Table 2).

Uranium occurs in a variety of minerals including zircon, apatite, and biotite, and in grain boundaries, mineral fractures, alteration products, and along the schistosity planes [29]. Granite and pegmatites, especially those produced from evolved magmas, are richer in U than mafic igneous rocks. Therefore, High

U values indicate the presence of felsic rocks, especially intrusives. Like U, Th it is a radioactive element, strongly lithophilic, and is more abundant in crustal rocks than in meteorites and mantle-type rocks. It forms several minerals including monazite (Ce, La, Nd, Th)(PO₄,SiO₄), the rarer thorite ThSiO₄ and thorianite ThO₂. Thorium acts similarly to Uranium which is generally higher in granitic than mafic igneous rocks [20]. Those facts explain the very strong associations of Th-U (0.99) and U- Σ REE (0.99)

Monazites are detected in tin mining locations along Granitic Belt of Southeast Asia, such as Phuket (Thailand) [33]. At least four kinds of monazite are known depending on relative elemental composition of the mineral: monazite-Ce (Ce, La, Pr, Nd, Th, Y)PO₄, monazite-La (La, Ce, Nd, Pr)PO₄, monazite-Nd (Nd, La, Ce, Pr)PO₄, and monazite-Sm (Sm, Gd, Ce, Th)PO₄. Tailings in Lingga were most possibly containing monazite based on regional geology and element contents [28]. The high Ce, La, and Th contents might indicate the presence of monazite as was also denoted in stream sediments from southern Cameroon [4]. Ce and La are the two most abundant REE in average both in Lingga and Singkep stream sediments (Table 3). Thorium are associate very strongly to Ce and La in Lingga samples with correlation values of 0.99 and ≈ 1 respectively to conclude that monazite-La might become the major variety of monazite. Moreover, very strong correlation of Th to Σ REE ($r = 0.99$) suggests that thorium bearing mineral, especially monazite-La, is the main REE source of the selected samples. Figure 4 draws the relation of Th and REE in Lingga samples. Monazites were characterized in the study about tin mines correlation and heavy detrital minerals from Peninsular Malaysia [34,35]. Moreover, on

radioactive prospecting of Muncung Granite at Singkep, [36] revealed that monazite and zircon are the most abundant in the felsic rocks while monazite, zircon, and xenotime in the pan concentrate to approve this study.

In order to prevent Oddo–Harkins effect in drawing the spider diagrams, elemental value of samples in this study normalized to Upper Continental Crust (UCC) [37] and chondrite values [38]. Cs, Th, U, Tm, and Yb in Lingga samples are enriched relative to UCC whilst Rb, Ba, and Sr are depleted (Figure 5). Sr and Ba in particular are largely bound in the lattice of the feldspars [39]. The lowest Sr and Ba anomalies in the two islands were denoted in Muncung Granite region (SSL 80 of Lingga; and SSS 48 and SSS 50 of Singkep) to inform that minimum feldspars might detached from the granite and weathered to form clay minerals. Nevertheless, SSS 72 from Batu Berdaun is special as it exhibits >8 times Nb enrichment whilst other eight samples are depleted. Moreover, SSS 72 is the only stream sediment, which show positive Sr anomaly.

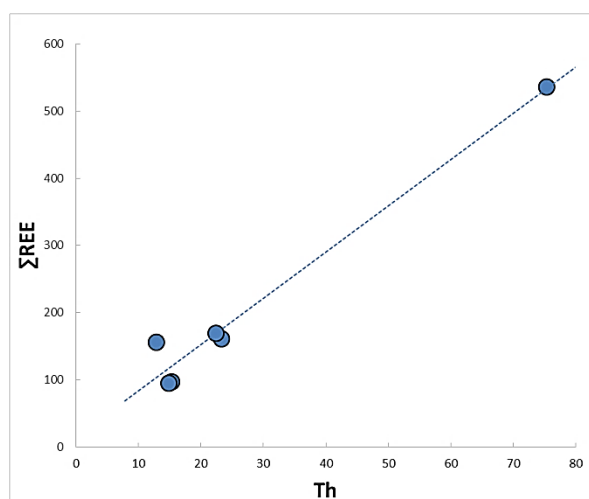


Figure 4. Th and total REE correlation of Lingga stream sediments. The very strong association is indicate on r value of 0.99.

The degrees of REE fractionation, expressed by (La/Lu)_N, of stream sediments

in this study are relatively low to intermediate. Lingga samples exhibit higher (La/Lu)_N in range of 4.27-9.34 (\bar{x} = 5.91) than Singkep's at 2.35-4.58 (\bar{x} = 3.11). Furthermore, LREE is intermediate to highly fractionated with (La/Eu)_N at 9.89-130.54 (\bar{x} = 52.59) whilst HREE is relatively flat (unfractionated) as (Gd/Lu)_N in the range of 0.44 to 1.4 (\bar{x} = 0.88). Among REE, the configuration of the 4f electron shell allows Ce and Eu to deviate from general 3+ valency [40]. Negative Ce anomaly (Ce/Ce* < 1) is shown in four samples, namely, SSL 32, SSL

78, SSL 48, and SSS 50 to inform that more Ce³⁺ of these samples was oxidized to Ce⁴⁺ than others (Figure 6). Eu negative anomaly is indicated in all selected samples with Eu/Eu* of 0.02 to 0.47. Because apatite is not commonly enriched in Eu relative to its nearest neighbors in the REE series (i.e., Sm and Gd), the negative Eu anomalies reported here are probably because of the absence of either detritus apatite or chemical weathering of apatite. This result implies that monazite is most possibly the main REE source in Lingga and Singkep.

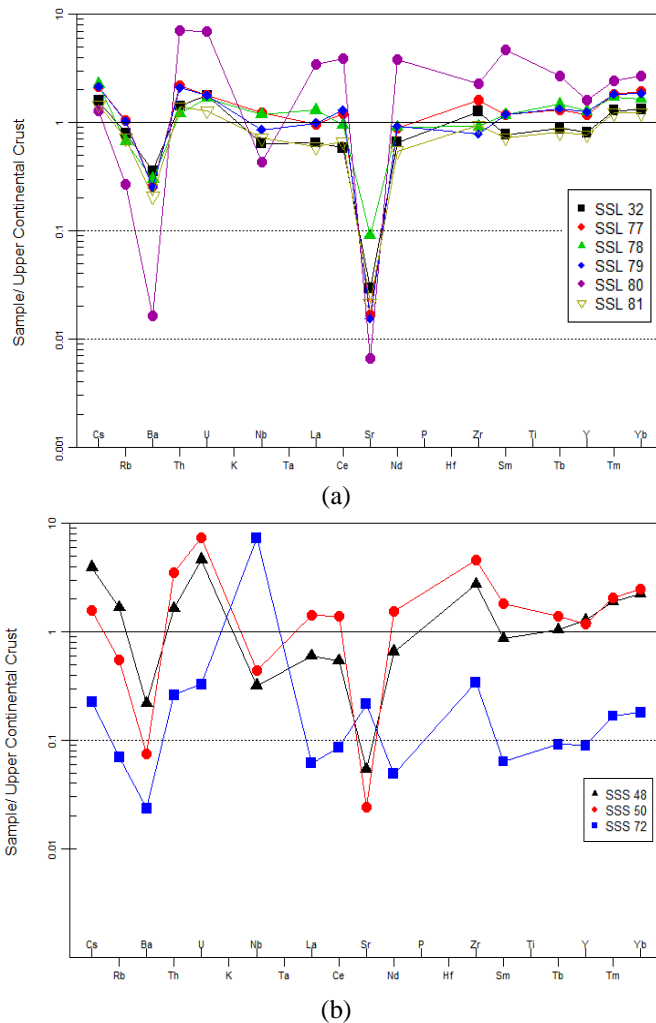


Figure 5. Upper Continental Crust normalized [37] of selected stream sediments: a) Lingga samples; and b) Singkep samples.

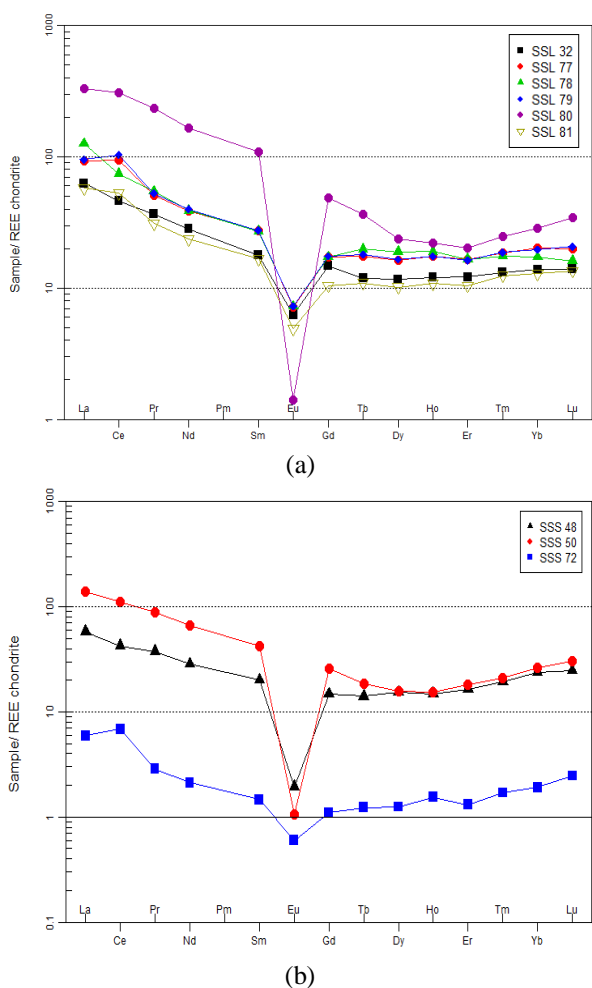


Figure 6. REE spider diagram of selected samples, normalized to chondrite value of [38]: a) Lingga samples; and b) Singkep samples

CONCLUSIONS

Nine selected stream sediments were identified megascopically and measured for the trace and rare earth elements composition by ICP-MS. Zr, Mn, Ba, and Rb are the most abundance elements in selected samples in Lingga whilst Zr, Mn, Cr, and Rb in Singkep. Fertilizers for agricultural area at Lingga most possibly contain As and Rb based on these elements abundances and association. Tin mine activity was found to influence the streambeds composition, especially in SSS 72 location. Very strong Th to \sum REE association suggests that thorium-bearing mineral, especially monazite-La, is the main REE source of the selected samples. All of the

studied samples exhibit Eu negative anomaly whilst negative Ce anomaly ($Ce/Ce^* < 1$) in four samples informs that more Ce^{3+} of these samples was oxidated to Ce^{4+} than others. The degrees of REE fractionation of stream sediments in this study are relatively low to intermediate with Lingga samples are more fractionated than Singkep. The interpretation of stream sediment geochemical is useful to be applied in other locations to reduce the overall cost of mineral exploration projects including Th- and U-bearing minerals.

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