



Reflectance spectroscopy and geochemical analysis of rare earth element-bearing tailings: A case study of two abandoned tin mine sites in Bangka Island, Indonesia

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ABSTRACT

Rare Earth Elements (REEs) are indispensable in the manufacturing of renewable energy and clean technologies. Due to the high demand for REEs, mine waste, called “tailings”, are sought because they could be a possible resource for REEs. In this study, tailing samples were collected from two tin mine tailings in Bangka Island, Indonesia, and analyzed using inductively coupled plasma optical emission spectrometry, x-ray powder diffraction, and Fourier transform infrared - attenuated total reflectance. Results showed that the tailing samples were identified as quartz and contained a high amount of erbium between 111.6 and 3768.4 µg/g. Absorption features in infrared reflectance spectra were related to REE concentrations. We found a positive correlation between erbium and two absorption features that have not been reported before: One feature is centered at 500 nm with a correlation of 0.685, and one is centered at 674 nm with a correlation of 0.829.

1. Introduction

The term “Rare Earth Elements (REEs)” refers to 17 elements in the periodic table (Weng et al., 2015). These are Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu), Scandium (Sc), and Yttrium (Y). All REEs occur in nature, except for Pm (MacMillan et al., 2017; Massari and Ruberti, 2013). Based on similarity in physical and chemical properties (Van Gosen et al., 2014), REEs can be divided into Light Rare Earth Elements (LREEs), which are Sc, La, Ce, Pr, Nd, Sm, and Eu and Heavy Rare Earth Elements (HREEs), which are Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y (Haque et al., 2014). REEs are currently critical ingredients in the manufacturing, for example, electric cars, wind turbines, energy efficient lights, and solar panels (Binnemans et al., 2013; Mancheri, 2012). Also, REEs are almost impossible to be found in nature as a pure REE compound (Weng et al., 2015).

Currently, REEs are mainly extracted from three REE-bearing minerals, namely monazite, xenotime, and bastnäsite (Jordens et al., 2013). These three minerals are commonly found in igneous rock such as granites, pegmatites, and carbonatites (Zepf, 2013), and account for more than 90% of the total REE resources (Weng et al., 2015). Monazite

(REE-PO₄) is an REE-bearing mineral rich in LREE containing 59.19–64.67 wt% of LREE and 0.61–5.48 wt% of HREE (Turner et al., 2016). Similar to monazite, bastnäsite (REECO₃F) is an LREE rich mineral containing 67.48–69.13 wt% of LREE and 0.09–0.7 wt% of HREE (Turner et al., 2014). Xenotime (REE-PO₄) is an REE-bearing mineral rich in HREE containing 0.5–1.45 wt% of LREE and 62.57–68.18 wt% of HREE (Turner et al., 2016).

REEs are often present in tailings (Binnemans and Jones, 2015; Falagán et al., 2017). Tailings refer to a residue of a mineral extraction process in which valuable elements are extracted from excavated materials in mining activity. In Europe, tailings have been identified as an REE resource which can be exploited without opening a new mine (Peelman et al., 2016). In Bangka Island, Indonesia, a study conducted by Szamalek et al. (2013) discovered that tailings contain 99% of quartz and 1% of other minerals, including monazite and xenotime.

REE-bearing tailings can be identified based on their infrared reflectance spectra. It is because REE ions have sharp absorption features in their Visible-Near Infrared (VNIR) reflectance spectra, originating from the 4f energy level of trivalent REE ions (Adams, 1965). The position of REE absorption features is mainly a function of specific coordination and asymmetry in the host crystal structure (Turner et al., 2016, 2014) and it may shift slightly due to the effect of neighboring ions (Adams, 1965). As shown in Fig. 1 and Table 1, Nd absorption

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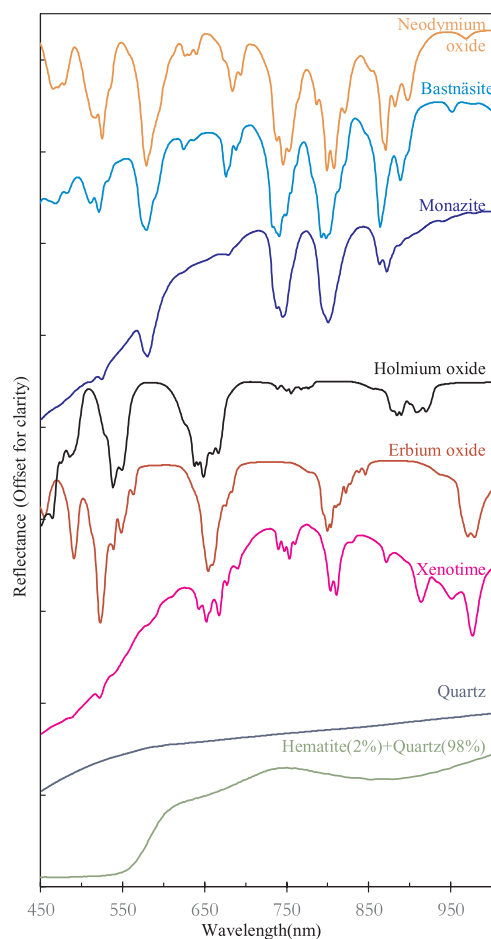


Fig. 1. Reflectance spectra of REE-bearing minerals, REE-oxides, quartz, and quartz contaminated by iron-bearing minerals in the VNIR wavelength range. Data source: Kokaly et al. (2017).

features are observed in Nd oxide, monazite, and bastnäsité, but are present at slightly different locations. Nd^{3+} in Nd oxides have a coordination number of 6 (Shannon, 1976), while REEs in monazite and bastnäsité have a coordination number of 9 (Jia et al., 2010; Unverfehrt et al., 2009). Also, each REE in an REE oxide and monazite is bound to 6 and 9 oxygens respectively, while in bastnäsité is bound to 6 oxygens and 3 fluorines. Meanwhile, the strength of REE absorption features is mainly a function of REE concentrations (Turner et al. (2016, 2014)). As summarized in Table 1, absorption features in monazite and bastnäsité spectra are mainly driven by Nd while in xenotime are mainly driven by Dy, Ho, and Er. This is because monazite and bastnäsité are rich in Nd whereas xenotime is rich in Dy, Ho, and Er.

Identifying REE-bearing tailings based on their reflectance spectroscopy is a challenging task. This is because iron (Fe) has absorption features in the VNIR wavelength range (Ben-Dor et al., 1999). Further, REEs are less abundant than Fe in the upper continental crust (Taylor and McLennan, 1995). Also, a study conducted by Wang et al. (2017) demonstrated that iron oxide absorption features dominated the reflectance spectra of REE-contaminated soils, and REE absorption features were not detected.

In this paper, we studied reflectance spectra of REE-bearing tailings collected from two abandoned tin mine sites on Bangka Island, Indonesia. REE concentrations in the collected tailing were quantified and linked to spectral variations in its spectral reflectance. The Fe concentration was also analyzed because it might mask REE absorption features.

Table 1

Absorption features of monazite, xenotime, and bastnäsité, and their probable origin. Data source is from Turner et al. (2016, 2014). Original data include the position, probable origin, and shape of the absorption features.

Monazite		Xenotime		Bastnäsité	
λ (nm)	Probable origin	λ (nm)	Probable origin	λ (nm)	Probable origin
575	Nd	634	Ho > Er	500	Nd
576	Nd	647	Ho, Er	511	Nd
579	Nd	651	Ho, Er	523	Nd
581	Nd	653	Ho, Er, U	533	Nd > Eu
584	Nd	657	Ho, Er	545	Nd
592	Nd, Pr	661	Ho, Er	557	Sm
622	Nd	665	Ho, Er	575	Nd
624	Nd	667	Ho, Er	580	Nd
625	Nd	668	Er > Ho	595	Nd > Pr
653	Ho, Er	678	Er > Ho, Nd	625	Nd
673	Nd	689	Er > Ho, Nd	636	Nd
676	Nd	692	Tm > Nd	642	Nd
679	Nd	740	Dy > Ho, Nd?	676	Nd
689	Nd	742	Dy > Ho, Nd?	681	Nd
734	Nd	747	Dy > Ho, Nd?	689	Nd
738	Nd	753	Dy > Ho, Nd?	693	Nd
745	Nd	760	Dy > Ho, Nd?	734	Nd
747	Nd	767	Nd?	738	Nd
749	Nd	781	Tm	741	Nd
757	Nd	803	Dy > Er, Nd?	749	Nd
770	Nd	811	Dy > Er, Nd?	755	Nd
792	Nd	817	Dy > Er, Nd?	761	Nd
796	Nd	822	Dy > Er, Nd?	768	Nd
800	Nd	823	Dy > Er, Nd?	781	Nd
804	Nd	826	Dy > Er, Nd?	784	Nd
814	Nd	828	Dy > Er, Nd?	792	Nd
830	Nd	872	Nd	797	Nd
863	Nd	876	Nd	803	Nd
871	Nd	877	Nd	813	Nd
877	Nd	896	Dy, Yb, Ho	821	Nd
887	Nd	909	Dy, Yb, Ho	845	Nd
896	Nd	914	Dy, Yb, Ho	864	Nd
906	Nd	920	Dy, Yb	871	Nd
941	Nd	932	Dy, Yb	889	Nd
957	Nd	951	Dy, Yb, Sm	898	Nd
980	Yb > Er	953	Dy, Yb, Sm	953	Sm

2. Study area and materials

The study area consisted of two abandoned mine sites located in Bangka Island, Indonesia (Fig. 2). Originally, there was a tin placer deposit in the study area, and from this deposit, tin ore (cassiterite) was extracted based on differences in specific gravity, leaving tailings. The produced tailings were accumulated in the two abandoned mine sites from which tailing samples were collected. Tailing samples were taken by pushing a 2-cm high and 2.2-cm diameter sample container into the surface (0–2 cm) of the two abandoned mine sites. 19 tailing samples were taken from the southeast study area, and 21 tailing samples from the northwest study area. In total, 40 tailing samples with a weight ranging from 1.32 g to 10.4 g each were collected and analyzed.

3. Methods

To determine the relationship between spectral absorption and REE concentration, the tailing samples were measured with an ASD spectrometer, and the REE concentrations were measured with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). All laboratory measurements were performed in the GeoScience Laboratory of the Faculty of Geo-information Science and Earth Observation, University of Twente. The spectral variations were related to REE concentrations using the Pearson correlation coefficient. All computation was performed in RStudio version 1.0.143 (RStudio Team, 2016).

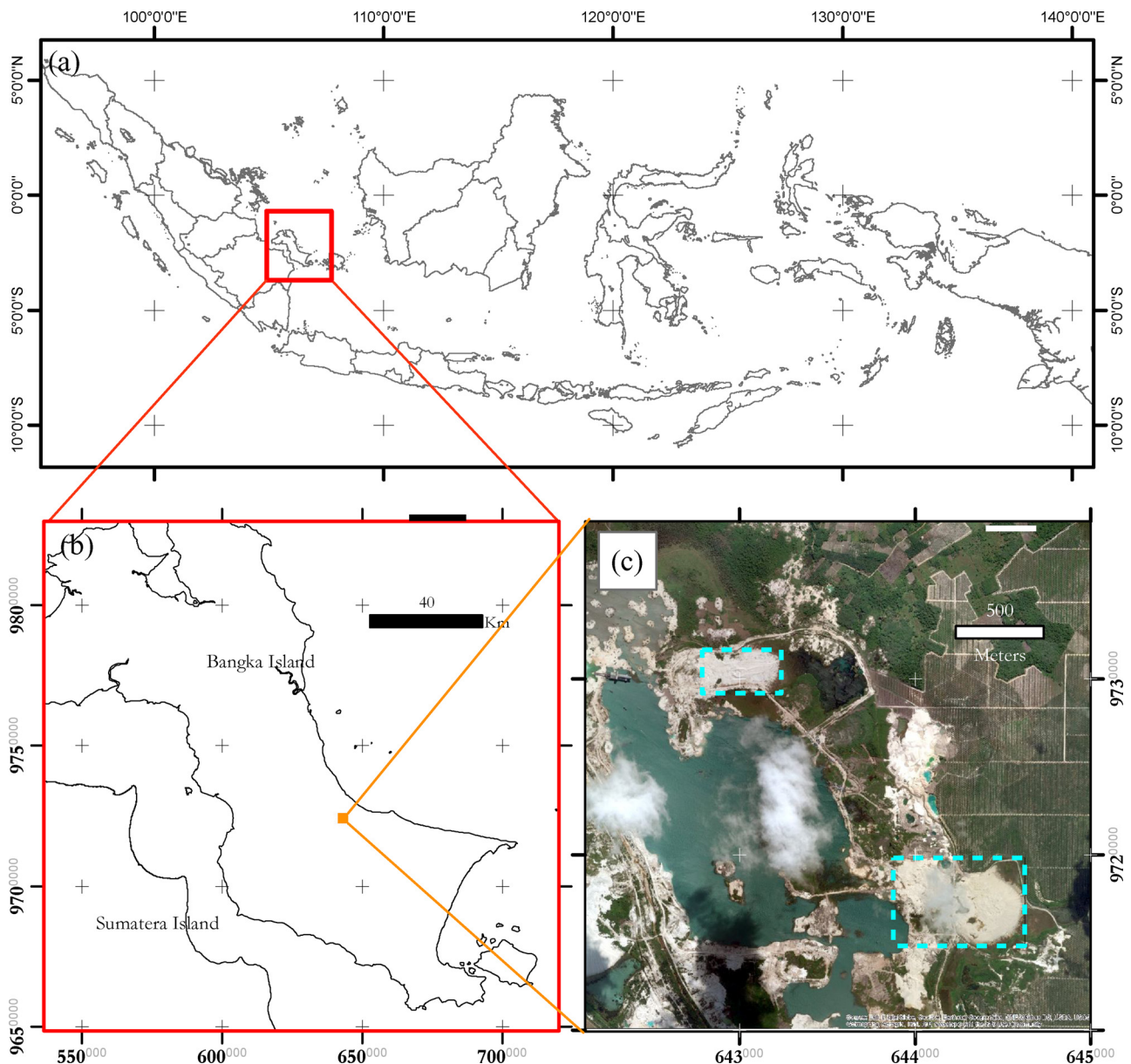


Fig. 2. (a) A map showing Indonesia and a red box indicating Bangka Island. (b) The location of two tin tailing wastelands in Bangka Island indicated by an orange box. (c) A zoom-in view of the orange box in (b), with the boundaries of the two tin tailing wastelands indicated by cyan-dashed boxes. The area of the two tin tailing wastelands is, combined, approximately 0.5 km². (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

3.1. Sample preparation and data acquisition

3.1.1. Spectral reflectance

Before measuring spectral reflectance, the samples were pulverized and sieved < 0.25 mm to homogenize the samples. The pulverized samples were poured in a 40 x 15 mm glass dish and their 350–1000 nm VNIR spectra were measured in a dark room using an ASD FieldSpec 3 with a high-intensity contact probe. Due to a relatively high noise level in the bands between 350–450 nm, the wavelength range of the spectra was subset to 451–1000 nm. To mitigate the effect of compositional heterogeneity of the samples, six measurements were averaged with the sample being shaken in between these measurements.

3.1.2. Elemental composition of REE and Fe

The concentration of REEs and Fe in the 40 samples was measured with a Perkin Elmer 8300DV ICP-OES. A borate fusion technique was used to convert the samples from solid to liquid phase:

- i 0.1gr of each pulverized sample was mixed with 0.8gr of an X-Ray flux, a mixture of 66% Li tetra- and 34% meta-borate (made by XRF Scientific Europe SPRL) in a platinum crucible.
- ii The platinum crucible was held for 6 min at 1150 °C inside an xRFuse 2 machine. These 6 min were divided into 3 min for melting the samples and 3 min for homogenizing melted samples by shaking the crucible.
- iii The melted sample was dissolved in 50 ml of 10% (v/v) supra pure HNO₃, ready for quantifying the total concentration of REEs and Fe in ICP-OES. Each sample was duplicated, and their precision was calculated using a relative percentage difference proposed by Popek (2013).

The calibration standards for REEs and Fe were made by diluting a standard solution with 10% (v/v) HNO₃ and 1.6gr (w/v) flux (1.6gr in 100 ml). The standard solution was TraceCERT reference material. Quality control was performed by measuring two known REE

Table 2

REE concentrations in tailing samples. All relative percentage difference values of duplicated samples were less than 30%. The number of samples with REEs above LOD (5 µg/g) are in the right-most column.

Elements	REE concentrations in 40 samples (unit in µg/g)			Relative percentage difference	N > LOD
	Min	Max	Mean		
Sc	5.2	238.2	36.2	18%	37
Y	5.8	255.6	51.5	24%	26
La	8.1	5502.4	285.1	27%	24
Ce	19.4	10700.3	367.9	27%	39
Nd	7.0	3903.3	150.1	28%	34
Sm	5.7	686.7	119.0	NA	7
Eu	16.3	16.3	16.3	NA	1
Gd	10.6	297.4	113.1	NA	3
Tb	6.0	24.0	11.4	NA	5
Dy	5.7	118.9	23.3	NA	12
Ho	13.3	13.3	13.3	NA	1
Er	111.6	3768.4	667.3	18%	40
Yb	5.7	29.1	12.8	NA	7
Lu	5.4	7.8	6.6	NA	2
Fe	135.3	3839.2	896.9	20%	40

The relative percentage difference is given by $[\text{Absolute } (a - b) / ((a + b) / 2)] \times 100$, where a and b are the concentration of a pair of duplicated samples. NA is not available and not calculated because REEs in most samples were below LOD.

concentration solutions measured at the middle and end of sample measurement.

3.1.3. X-ray diffraction and infrared absorbance spectra

Five randomly-selected samples were analyzed using X-ray Powder Diffraction (XRD) technique for mineral identification. XRD measurements were carried out on a Bruker D2 Phaser XRD. 2θ was started from 6 to 80 degrees with an increment of 0.012°. The effective total time was set at 662.5 s, and the measurement was repeated once. Divergence slit, knife, and detector slit were adjusted at 1 mm, 1 mm, and 8 mm respectively. The EVA software package that is shipped with the Bruker D2 Phaser XRD instrument was used for interpreting the XRD diffractogram. Infrared absorbance spectra of 40 samples were analyzed using Fourier Transform Infrared - Attenuated Total Reflectance (FTIR-ATR) technique to measure functional groups. FTIR-ATR analysis was performed using a Bruker Vertex FTIR spectrometer equipped with Pt-ATR-diamond accessory. The absorbance was between 4000 cm⁻¹ to 600 cm⁻¹ was analyzed, with a resolution and sample scan time set at 4 cm⁻¹ and 16 scans respectively. The obtained infrared absorbance spectra were compared visually to infrared absorbance spectra published by Lafuente et al. (2015).

3.2. Data analysis

3.2.1. Identifying REE concentration anomalies

REE concentrations were normalized by dividing them with REE chondritic abundance (O'Neill, 2016). It is important because if not normalized, REE concentrations will appear in a zigzag pattern in a line graph of REE concentration, making it difficult to recognize an anomaly of REE concentrations. Chondritic abundance refers to the theoretical abundance of an element date back to when the universe is formed (Rollison, 1993). For the present study, we used REE chondritic abundance provided by Anders and Grevesse (1989).

To identify whether REE concentrations in the samples have an anomaly or not, REE concentrations in the samples were normalized and compared to REE concentrations in the Upper Continental Crust (UCC) provided by Taylor and McLennan (1995) and processed REE ore from Mount Pass REE mining provided by Castor (2008). Every graph above the graph of the normalized REE concentration in the UCC

indicates enrichment, while below the graph indicates depletion.

3.2.2. Derivation of spectral parameters

To link REE concentration to variations in spectral absorption, three spectral parameters were defined to express the changes in absorption features: band ratios, absorption band depth, and absorption band area. Band ratio is the ratio between 550 nm and 500 nm ($R_{550/500}$) and between 712 nm and 674 nm ($R_{712/674}$). Absorption band depth is the depth of absorption feature at 500 nm (D_{500}) and 674 nm (D_{674}). Absorption band area is the area of absorption features between 450 nm and 550 nm ($A_{450-550}$) and between 600 nm and 712 nm ($A_{600-712}$).

During measuring reflectance spectra of the samples, the viewing geometry of ASD FieldSpec 3 was constant, but the surface of the sample being measured was not always flat. This caused spectral variations in overall albedo, and the spectral variations were suppressed by performing a band ratio operation on the reflectance spectra while detecting diagnostic absorption features (Crowley et al., 1989; Rowan et al., 1974). For computing absorption band depth and area, a continuum-removal technique proposed by Clark et al. (1987) was applied to normalize albedo differences. Continuum removal was performed by division rather than subtraction to prevent shifts in band positions (Clark and King, 1987).

3.2.3. Statistical analysis

The relationships between REEs and Fe were assessed using the Pearson correlation. The Pearson correlation was also used to assess the relationships between REEs and spectral absorption parameters. The correlation coefficient was produced at a 99% confidence level (2-tail).

3.2.4. Spectra interpretation

The obtained spectra were compared visually to published spectra of REE-oxide and REE-bearing minerals as shown in Fig. 1 (Kokaly et al., 2017) as well as a study conducted by Turner et al. (2016) to interpret absorption features.

4. Results

4.1. REE and Fe concentrations

The REE and Fe concentration in the samples are summarized in Table 2. Due to severe signal interference, the Limit of Detection (LOD) value for all REEs in this study is 5 µg/g and 0.5 µg/g for Fe. In most samples, the concentrations of REEs were below LOD. The exception was Er concentration, which ranges from 111.6 µg/g to 3768 µg/g. Pm was not quantified because it does not occur in nature (MacMillan et al., 2017; Massari and Ruberti, 2013). Pr and Tm were not reported because their signal intensity measured in ICP-OES experienced severe signal interference. All estimated relative percentage difference values were less than 30%.

Fig. 4 shows the normalized REE concentrations in the samples compared to the normalized REE concentrations in UCC and processed REE ore of the Mount Pass mine site. The normalized REE concentrations in the samples were higher than REE abundances in UCC, indicating enrichment, and the concentration of Er in the samples exceeded the Er concentration in the processed REE ore from the Mount Pass mine site.

4.2. Spectral reflectance, XRD, and FTIR-ATR result

Fig. 5 shows the spectral reflectance of the samples compared to the reflectance spectra of REE-oxide, quartz, and xenotime. It can be seen that two absorption features at around 500 nm and 674 nm were present in the sample spectrum. The 674 nm absorption feature in the sample spectra is next to the absorption feature centered at around 651 nm in Ho oxide, Er oxide and xenotime spectra indicated by a yellowish shaded area shown in Fig. 5. Fig. 6 shows spectral variations

Table 3

Pearson correlation coefficient among REE concentrations in the samples. Green-colored cells indicate a correlation between LREEs, while orange-colored cells indicate a correlation between HREEs. (For interpretation of the references to colour in this table legend, the reader is referred to the web version of this article).

Element		Log(Sc)	Log(La)	Log(Nd)	Log(Ce)	Log(Y)	Log(Er)
Log(La)	r	0.808**					
	N	23					
Log(Nd)	r	0.720**	0.971**				
	N	32	18				
Log(Ce)	r	0.757**	0.967**	0.973**			
	N	37	23	34			
Log(Y)	r	0.807**	0.639**	0.593**	0.562**		
	N	25	16	25	26		
Log(Er)	r	0.613**	0.228	0.163	0.179	0.800**	
	N	37	24	34	39	26	
Log(Fe)	r	0.637**	0.358	0.289	0.315	0.825**	0.863**
	N	37	24	34	39	26	40

**Correlation is significant at the 0.01 level (2-tailed) r is the correlation value N is numbers of samples.

with changing in Er concentration. The depth of 674 nm absorption feature decreases as Er concentration in the sample decreases. Fig. 7 shows the diffractogram and infrared absorbance spectra of the samples.

4.3. Statistical correlation between REEs and Fe

The correlations between REEs and Fe are summarized in Table 3. Only statistical correlations between Sc, La, Nd, Ce, Y, Er, and Fe could be defined because Sm, Eu, Dy, Ho, Yb, and Lu concentrations were below LOD in most samples. From Table 3, LREEs (Sc, La, Ce, and Nd) have a strong correlation when they are in pairs among them, while Er shows the strongest correlation with Fe and Y.

4.4. Statistical correlation between REE concentrations and spectral variation

Three spectral parameters (band ratio, band depth, and band area) were derived from variations in absorption bands. Their correlation with REEs and Fe concentrations is shown in Table 4. All three parameters appeared to have no significant correlation with Sc, La, Ce, and Nd concentration. The Er concentration had the strongest relationship with band $R_{712/674}$, D_{674} , and $A_{600-712}$ with R-values of 0.829, 0.689, and 0.71 respectively.

5. Discussion

Of all REEs under investigation in this study, Er had the highest concentration which varied between 111.65 µg/g and 3768.45 µg/g. Compared to other REEs, whose concentrations are below LOD (5 µg/g), the amount of Er in the samples was even higher than Er concentrations in the processed ore from the Mount Pass REE mine. This finding was unexpected because in nature the abundance of Er is sparse compared to most other REEs (Fig. 3). It remained unclear what the reason for this enrichment is, and to date, no study has discussed the enrichment of Er in Quartz whether in the study area or elsewhere. All samples were analyzed using FTIR-ATR technique, and the obtained infrared absorbance spectra matched with quartz infrared absorbance

spectra published by Lafuente et al. (2015). Five samples were analyzed using XRD technique, and their diffractogram was matched with the diffractogram of quartz in the database of EVA (Bruker) software. It can be seen that both the results of FTIR-ATR and XRD are in agreement with each other.

Xenotime is one of the most common REE-bearing minerals, and we expected to encounter it in this study. However, from the result of the XRD and FTIR-ATR analyses, tailing samples were identified as quartz. A possible explanation why xenotime was not detected, is because it was extracted during the mining operation. As a result, no xenotime remains in the tailings. To prove, we can calculate a “concentration criterion” between cassiterite and quartz, between xenotime and quartz, and between cassiterite and xenotime. The concentration criterion is an indicator of how effective two materials can be separated based on their specific gravity. The concentration criterion between the two materials must be at least 2.5 to separate them (Brits, 1991). In our study area, tin ore (cassiterite) was separated from tailings based on differences in specific gravity. Given the specific gravities of cassiterite (7.0), xenotime (5.1), and quartz (2.6) (Vernilli et al., 2007; Wadell, 1935; Wyslouzil, 1990), concentration criteria between cassiterite and quartz is 3.75, between xenotime and quartz is 2.56, and between cassiterite and xenotime is 1.46. It can be seen that when cassiterite, xenotime, and quartz were present and separated together, cassiterite and xenotime will be separated from quartz, but xenotime cannot be separated from cassiterite. This means that the xenotime was extracted together with cassiterite, leaving quartz. Furthermore, Szamalek et al. (2013) found xenotime together with cassiterite extracted from tin placer deposit in Bangka Island.

The obtained spectra were compared to USGS mineral spectral library (Kokaly et al., 2017), and the 500 nm absorption feature matched iron oxide absorption feature. However, Er is a more plausible source of the 500 nm absorption feature than Fe and Y due to several reasons. First, the highest Fe concentration in the sample is only 3839.25 µg/g, and the mean of Fe concentrations is 896.9 µg/g. This amount is not sufficient to produce absorption features because it is too low compared to Fe concentration in the mixture of hematite (2% or approximately 14,000 µg/g of Fe) and quartz (98%) shown in Fig. 1. Second, the 500 nm absorption feature had the highest correlation coefficients with

Table 4

Pearson correlation coefficients between spectral parameters and REE concentrations (on a logarithmic scale). Green-colored cells indicate correlation coefficients of more than 0.5. (For interpretation of the references to colour in this table legend, the reader is referred to the web version of this article).

Element	log (R _{550/500})	log (D ₅₀₀)	log (A ₄₅₀₋₅₅₀)	log (R _{712/674})	log (D ₆₇₄)	log (A ₆₀₀₋₇₁₂)
log(Sc) N=37	0.181	0.125	0.151	0.296	0.177	0.207
log(Y) N=26	0.520**	0.540**	0.572**	0.545**	0.489*	0.484*
log(La) N=24	0.01	-0.008	-0.015	-0.001	0.042	0.048
log(Ce) N=39	-0.078	-0.097	-0.088	-0.091	-0.137	-0.12
log(Nd) N=34	0.011	0.037	0.028	-0.036	-0.053	-0.052
log(Er) N=40	0.685**	0.604**	0.640**	0.829**	0.689**	0.710**
log(Fe) N=40	0.683**	0.552**	0.593**	0.736**	0.521**	0.552**

**Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed) N is numbers of samples.

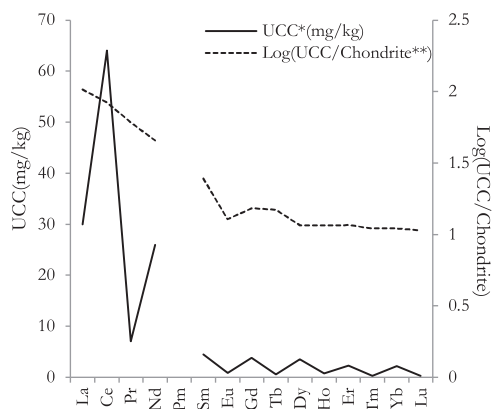


Fig. 3. REE concentrations in the UCC and chondrite normalization of REE in the UCC. In nature, the abundance of REEs follows the Oddo-Harkins rule, which appears as a zigzag pattern in a diagram of REE concentrations, as illustrated by a solid line. REE concentrations in the UCC are normalized to eliminate this zigzag pattern, and the line graph of REE concentration in the UCC appears smooth after the normalization as illustrated by the dashed line. The normalized REE concentration in the UCC is used as a comparison to REE concentration (after normalization) in the tailing sample. When the line graph of the normalized REE concentration in tailings samples is above the line graph of the normalized REE concentration in the UCC, this indicates enrichment of REE concentration. When the line graph of the normalized REE concentration in tailings samples is below the line graph of the normalized REE concentration in the UCC, this indicates depletion of REE concentration. Data source: (*) Taylor and McLennan (1995) and (**) from Anders and Grevesse (1989).

Er, followed by Fe and Y (Table 4). Third, Y cannot be the source of the 500 nm absorption feature because trivalent ions of Y do not produce absorption features in the VNIR wavelength range. Y correlates with the 500 nm absorption features because Y is correlated with Er. This type of correlation is called a “spurious correlation” Lewis-Beck et al. (2004).

There were no spectra of USGS mineral spectral library (Kokaly et al., 2017) matched the 674 nm absorption feature in the sample spectra. Nevertheless, several results asserted that the 674 nm absorption feature is due to the presence of Er. Er has absorption features at around 674 nm. As shown in Fig. 1 and summarized in Table 1, the position of Er absorption features is not fixed but varied between 634 nm and 689 nm. This variation is due to differences in the coordination number in the host crystal structure (Turner et al. (2016, 2014)). Each Er ion in Er oxide, monazite, and xenotime (an REE phosphate) has 6, 9, and 8 coordination numbers respectively. In all these molecules, Er is bound to oxygen. In all these molecules Er is

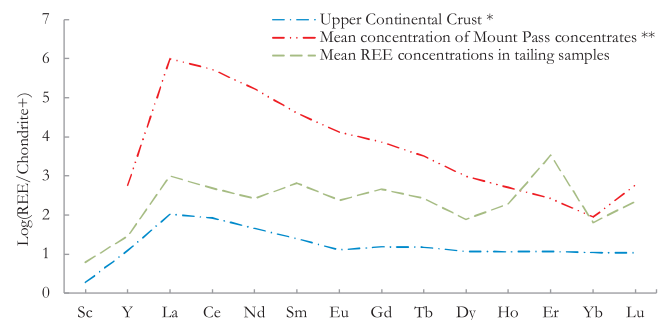


Fig. 4. Chondrite-normalized distribution of the mean REE concentrations compared to the upper continental crust and Mount Pass concentrates. The average of REE concentrations in tailing samples indicated by a green-dashed line is above the abundance of REEs in Upper Continental Crust (a blue-dashed line), meaning there is the enrichment of REEs in the tailing samples. The Er concentration in the samples exceeds that in the processed ore from Mount Pass mine sites (a red-dashed line). Data sources: (+) from Anders and Grevesse (1989), (*) from Taylor and McLennan (1995), (**) from Castor (2008). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

bound to oxygen responsible for producing absorption features around 674 nm: at 651 nm in Er₂O₃, at 653 nm in monazite and 634–689 nm in xenotime, as seen in Fig. 1 and Table 1. Most likely Er ions in our investigation are incorporated into quartz crystal structure resulting in different coordination numbers and ligands, which are still unknown and hence produce an unknown characteristic absorption feature.

The strength of REE absorption features is mainly a function of REE concentration (Turner et al. (2016, 2014)). As summarized in Table 1, REE absorption features in monazite and xenotime spectra are primarily driven by their characteristic REEs and their concentrations within the mineral. In our samples, Er had the highest mean concentration of 667.3 µg/g, while the mean concentrations of other REEs were between 367.9 µg/g and 6.6 µg/g (Table 2). Of REEs, Ho also has absorption features at around 674 nm; however, the Ho concentrations in 39 out of 40 samples are less than LOD. Hence, considering our found Er concentration together with the position of Er absorption features found in literature, Er is the best candidate for the 674 nm absorption feature. Furthermore, why only Er can be the source of 674 nm absorption feature is because Er, of all elements under investigation, had the strongest correlation with band R_{712/674}, D₆₇₄, and A₆₀₀₋₇₁₂ with R-values of 0.829, 0.689, and 0.71 respectively.

Several studies have been conducted to target REE using airborne and satellite remote sensing (e.g., Bedini, 2009; Rowan and Mars, 2003;

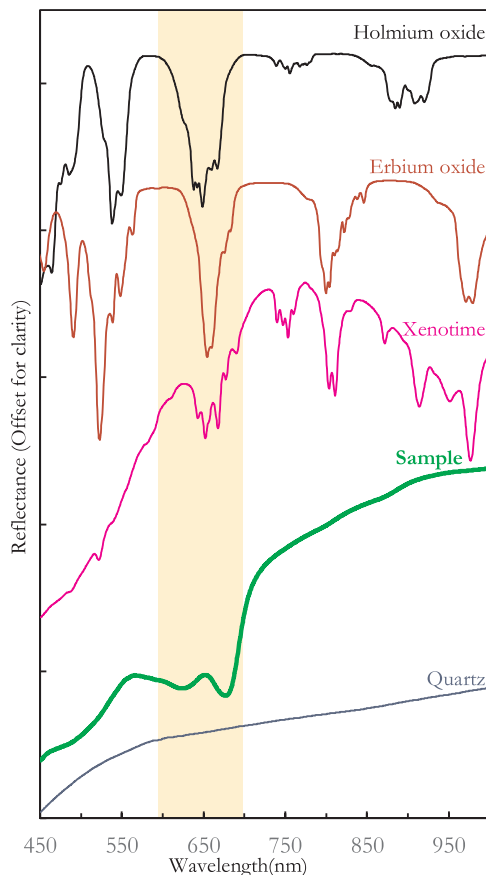


Fig. 5. Reflectance spectra of a Bangka Island sample, compared to Ho oxide, Er oxide, xenotime and quartz spectra. The yellowish shaded area indicates diagnostic absorption features.

Zimmermann et al., 2016). These studies used Nd-related absorption features as a pathfinder to discover REE because of all REEs, Nd exhibits absorption features at around 583 nm, 744 nm, 802 nm, and 871 nm (Neave et al., 2016). However, only the study conducted by Rowan and Mars (2003) succeeded in detecting Nd-related absorption features. Our results indicate that Er produces absorption features at around 674 nm when it attached in quartz. This means that it might be possible to use the Er absorption features to target REE-bearing tailings with remote sensing. We expect that airborne hyperspectral sensors but also and several multi-spectral satellite sensors with sufficient, relatively narrow, bands in the VNIR wavelength region might be capable of

detecting the Er absorption features. Examples of such sensors would be Sentinel-2 MSI and WorldView 2–4, although additional research is required to confirm this.

6. Conclusion

Tailings from abandoned tin mine sites in Bangka Islands were collected and analyzed using ICP-OES, XRD, and FTIR-ATR. By using ICP-OES, we identified a high anomaly of Er concentration reaching up to 3768.4 $\mu\text{g/g}$ in tailing samples. Based on the results of the XRD and FTIR-ATR analyses, tailing samples were identified as quartz. Therefore, we concluded that our tailing samples were REE-enriched quartz, but the reason behind this enrichment remains unknown. It was expected to find xenotime in tailing samples, but due to mineral extraction during mining operation, it was probably extracted together with tin ore.

Two absorption features at around 500 nm and 674 nm were observed in the reflectance spectra of the tailing samples. Three spectral parameters (band ratio, absorption band depth, and absorption band) were derived from both absorption features and had strong correlations with Er with correlation coefficients varied between 0.604 and 0.829. Considering correlation coefficients coupled with the position of Er absorption features (in Er oxide and xenotime spectra) and Er concentration in the tailing samples, we concluded that both absorption features are due to the presence of Er. Both absorption features might be due to Fe, but results show that it is most unlikely due to Fe because the concentration of Fe is too low in the tailing samples less than 3839.2 $\mu\text{g/g}$.

This study has also shown that the absorption feature related to REEs can shift when REE ions are incorporated into different minerals. Further research is required to investigate the enrichment of REE especially Er in the samples, and the coordination complex of Er in quartz crystal structure.

It is also worth a try to investigate whether both Er absorption features can be detected using airborne or satellite remote sensing as the success rate of detecting Nd-related absorption feature is low. If successful, then it can be an alternative to detect REEs using remote sensing technique because so far, only one study detected Nd-related absorption features in an airborne remote sensing image.

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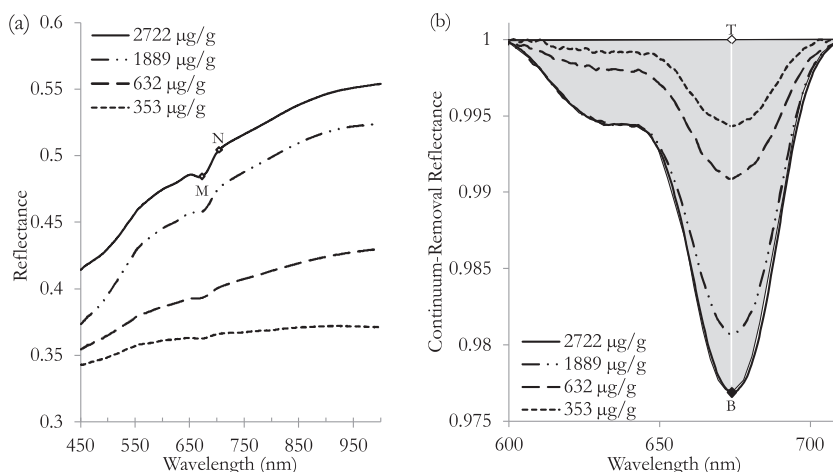


Fig. 6. Variation in the VNIR spectra of the Bangka Island samples, with Er concentration ranging from 353 to 2722 $\mu\text{g/g}$. a) the Band ratio measure is the ratio between the reflectance values at 712 nm and 674 nm (N/M). b) The Band depth measure is the difference value between T and B, and the band area is the grey shaded color.

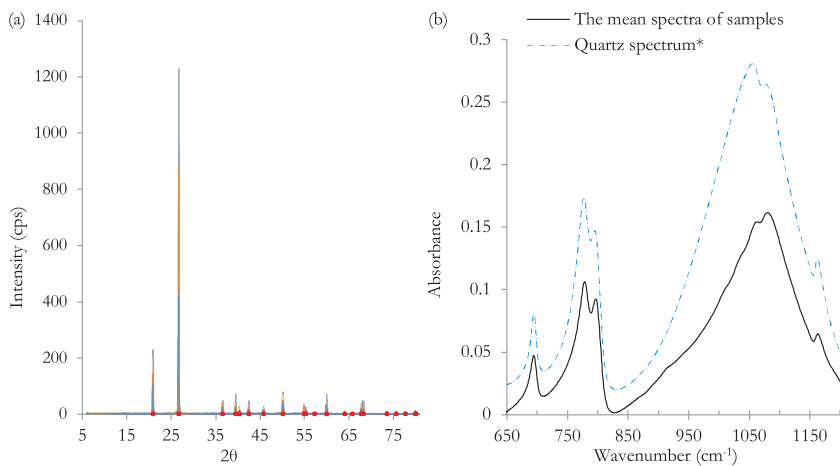


Fig. 7. The diffractogram and infrared absorbance spectra of the samples. a) The peak positions of quartz are indicated by red dots, which match the peak positions of the sample. Peak positions are resulted from the distance between planes of atoms within a crystalline and are unique for each mineral, and can be used as a fingerprint to identify minerals. Sharp peaks indicate crystalline materials. b) The mean FTIR-ATR infrared absorbance spectra of a sample compared to that of quartz. Source of the quartz spectrum (*) is from Lafuente et al. (2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

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