DETERMINATION OF HEAVY MINERALS IN 'AMANG' FROM KAMPUNG GAJAH EX-MINING AREA

(Penentuan Mineral Berat Dalam 'Amang' Dari Kawasan Bekas Lombong Kampung Gajah)

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Abstract

'Amang' known as a tin tailing, was left abundant in ex-mining area. It is rich in heavy minerals containing rare earth elements. Rare earth elements have various applications in different types of industries. In this study, Kinta Valley in the State of Perak was chosen as the study area because it used to be an active and the largest tin mine. The aim of this study is to measure the amount of rare earth present in these heavy minerals i.e. ilmenite and monazite. Soil samples containing `amang` were taken to recover its heavy minerals by separating them into individual minerals. The separation involves a gravitational separation and magnetic separation using large volume of water and strong hand magnet respectively. Sample containing monazite, ilmenite, and zircon were separated by 8000 G hand magnet. The morphology of each mineral was investigated by computer controlled scanning electron microscopy coupled with an energy-dispersive X-ray detector (CC-SEM/EDX). Surface morphology studies from SEM show that most samples are rounded to subrounded. The minerals were digested using microwave digestion system, and then measured for its rare earth elemental content using inductively couple plasma-optical emission spectroscopy (ICP-OES). The results show that soil and sediment in this study area contain heavy minerals monozite, ilminite and zircon. The separation method chosen for this study work well and the minerals were confirmed by SEM/EDX results. ICP-OES give the rare earth elements content of these minerals.

Keywords*:* Heavy minerals, 'amang', rare earth element (REE), CC-SEM/EDX, ICP-OES

Abstrak

Amang adalah tahi bijih timah, yang banyak terdapat dikawasan bekas lombong timah. Ianya kaya dengan mineral berat yang mengandungi unsur nadir bumi. Unsur nadir bumi mempunyai banyak kegunaan di dalam pelbagai industri. Dalam kajian ini, Lembah Kinta di Negeri Perak telah dipilih sebagai kawasan kajian kerana kawasan ini pernah menjadi kawasan terbesar dan aktif perlombongan bijih timah suatu ketika dahulu. Tujuan kajian ini adalah untuk mengukur amaun unsur nadir yang hadir di dalam mineral berat iaitu ilminite dan monazite. Sampel tanah yang mengandungi amang telah di ambil untuk dipisahkan kepada mineral berat yang berbeda. Pemisahan melibatkan pemisahan graviti menggunakan isipadu air yang besar dan pemisahan magnet menggunakan magnet tangan yang kuat. Sampel yang mengandungi monazite, ilminite dan zircon telah dipisahkan menggunakan magnet tangan 8000 G. Morfologi setiap mineral telah dikaji menggunakan mikroskop imbasan elekron berpasangan dengan pendarflor sinar-X serakan tenaga kawalan komputer (CC-SEM/EDX). Morfologi permukaan dari SEM menunjukkan kebanyakan sampel adalah bulat atau separa bulat. Mineral telah dihadamkan menggunakan sistem ketuhar mikro, dan kemudian di ukur menggunakan spektroskopi plasma aruhan pendua – pancaran optik (ICP-OES). Hasil kajian ini menunjukkan sampel tanah dan sedimen mengandungi mineral berat monazite, ilminite dan zircon. Kaedah pemisahan yang dipilih untuk kajian ini adalah bersesuaian dan mineral telah disahkan melalui hasil analisis SEM/EDX. ICP-OES memberikan kandungan unsur nadir bumi dalam mineral yang terhasil.

Kata kunci: mineral berat, amang, unsur nadir bumi, CC-SEM/EDX, ICP-OES

Introduction

Former tin mining areas normally rich in ‘amang’, the tin tailing that contained heavy minerals which in turn will be economically beneficial to the mineral industries. Other researchers found that beach sand [1] and rock [2] are mineral resources other than ex mining area. A mineral is a naturally occurring substance formed through geological processes that has a characteristic chemical composition, a highly ordered atomic structure and specific physical properties. Heavy minerals refers to minerals with a specific gravity (SG) greater than that of quartz (SG = 2.7) [3]. Some heavy minerals like monazite ([Ce, La, Nd, Gd, Th] PO_4), zircon ($ZrSiO_4$), ilmenite ($FeOTiO_2$), xenotime (YPO_4) and struverite ($Nb.Ta.TiO_2$) are used in minerals industries.

These valuable minerals have many uses in industries. Zircon is a valuable mineral used as raw material in various industries such as foundry, ceramics, and refractory. In Bangladesh approximately 300 tonnes of zirconium flour is consumed every year in ceramic industries; the entire amount being currently imported. However, zircon occurring in the Bangladesh coast has so far not been utilized [4]. Ilmenite fines is a by-products generated by the titanium slag and iron industries consisting of titanium dioxide, which is commonly used for the manufacture of white pigment for paint, plastic, paper and fabrics [5].

The rare earth elements are recovered through the separation of certain rare earth oxide bearing minerals, including bastnasite, monazite and ionic clays. Rare earth elements (REEs), from lanthanum to lutetium, are a group of elements with similar chemical and physical properties due to their electronic configurations. REE are divided into two sub-groups: the light rare earth elements (LREEs) from La to Sm and heavy rare earth elements (HREEs) from Gd to Lu [6]. Gadolinium oxide (GdO_2) is used for many different high technology applications such as infrared absorbing automotive glass, petroleum cracking catalyst, used in microwave applications, and colour TV tube phosphors while europium is responsible for the red color in television screens and computer monitors [7, 8].

During the golden era of tin mining, Kampung Gajah in Perak, (N04º 14.967´ E101º 02.420´) used to be one of those areas producing tin for exporting purposes. Tin ores were processed using a physical property (wet separation technique or smelting process) to recover the tin. The remaining (‘amang’) were left there since not many people knew their uses. \`Amang\` is a widely accepted term in Malaysia for the heavy mineral rejects which remain after tin oxide (cassiterite) has been extracted from tin ores [9].

Nowaday, ‘amang’ is becoming more important since we can recover valuable heavy minerals from it. The concentration of heavy minerals from amang or soil contain rich amang involves a gravitational separation process or floatation, which will produce a layer which can be easily differentiated from mud and sand. The more density of the materials, the deeper they will sink. By applying this concept, the dense material which is minerals will sink while others will float. Magnetic separation process may produce two distinct fractions which are magnetic minerals and non magnetic minerals [1]. Magnetic minerals would consist of ilmenite only while non-magnetic minerals consist of xenotime, monazite and zircon [10, 3].

This study was conducted in order to design the lab scale method for physical separation of minerals from ‘amang’ enriched soils and sediments. The aim was to find the percent recovery of the minerals found in each sample from different locations and to determine the morphology of the minerals. From the percent of mineral recovery, one can estimate which location possessed high amount of heavy mineral concentration. SEM/EDX analysis was used the check the morphology and the elemental composition of the rare earths presents in the samples while results from ICP-OES shows the concentration of selected rare earths in the sample.

Experimental

Sampling

The sampling area is an abundant mine lake which is connected to other lakes in the area. This lake is adjacent to the soil sampling location. Both areas used to be the place for tin ores processing and rich with \`amang\`. About 2 kg of soil samples were collected from each sampling point in three different depths (0-6, 6-12, and 12-81 cm) using hand auger. Sediment samples were collected using gravity corer at various points in the lake. The samples were packed in a plastic bag and brought back to the laboratory. The samples were cleaned with water [11] which actually helped in the separation, involving differences in size and weights of these minerals since the densest material will move to the bottom hence producing a few layer differentiated them into mineral, sand and mud. Soils and sediments were kept for an hour in a container after washing with water, and then the lighter layer will floated and discarded, leaving behind the densest material. Samples were then dried in an oven at 70ºC, sieved and the heavy mineral concentrates were then separated into different individual mineral fractions using a permanent hand magnet [11].

Microwave digestion of samples for ICP-OES analysis.

The digestion of mineral sample for ICP-OES analysis was undertaken in Teflon high pressure vessels using a microwave oven with temperature and pressure controls. 0.5 grams of sample was weighed into a microwave vessel with 9 mL and 3 mL of hydrochloric acid and nitric acid respectively. After digestion, the solution was carefully collected by filtering using Whatman paper no. 4. Then, the samples were diluted to a final volume of 100 mL using Milli-Q water from a Milli-Q-system (NANO pure Diamond, Barnstead). Throughtout the experiment, all the polypropylene bottles and glasswares used for preparation and storing the solutions were immersed in a dilute HNO_3 solution overnight, then cleaned with purified water and finally dried [12].

Stock solutions of Lanthanum, Gadolinium, Lutetium, Scandium and Dysprosium of 1000 mg/L (High-Purity Standards) were used to prepare the standards solutions for the calibration curves for ICP-OES.

Morphology and Elemental Composition of Heavy Minerals

Morphological examinations of mineral grains were performed using a scanning electron microscope (Philip XL40). Samples were prepared by mounting several grains of each sample on aluminum stubs using double sided tape The samples were coated using gold sputter before undergo grain analysis. The elemental compositions of selected grains were determined by energy dispersive X-ray analysis (EDX) on 2 or more areas of each grain to minimize errors.

Results and discussion

Tables 1 and 2 show the minerals recovery after a wet and magnetic separations of soils samples, respectively. The percent recovery varies for all sampling points since the minerals content will depend on the amount of ‘amang’ present in the soil. Samples from locations C and D have more than 40 percent mineral recovery with D11 has the highest recoverey. Location A12 also has the recovery of more than 40 percent. There is no regular patern for the mineral content in the soils. In general, zircon content in amang is higher than ilminite and monozite. The mineral accumulation may depend on the activity like smelting process previously, and they was not forming a uniform patern through out the area.

Table 1: Recovery of minerals from soils containing ’amang’ by wet gravity separation as percentage of raw sample

Sample(s)	mass (g)	wet separation (g)	percent recovery (%)
A11	1375.7	none	None
A21	1653.4	136.2	8.20
A12	1227.5	559.9	45.60
A22	5743.4	360.7	6.30
B01	2813.8	361.5	12.85
C11	2242.1	977.3	43.59
D11	6719.0	5200.2	77.40
D21	2797.5	1119.6	40.02

Table 2: Recovery of minerals from soils by magnetic separation as percentage of raw sample

Samples	monazite (g)	recovery (%)	ilmenite (g)	recovery (%)	zircon (g)	recovery (%)
A11	none	none	none	none	none	none
A21	77.0	4.7	32.6	1.9	2.9	0.2
A32	10.4	0.9	1.8	0.2	33.7	2.8
A42	30.7	0.5	18.9	0.3	18.9	0.3
B01	3.5	0.1	13.0	0.5	29.7	1.1
C11	11.8	0.5	15.0	0.7	44.1	1.9
D11	111.9	1.7	4142.6	61.7	18.0	0.3
D21	7.1	0.3	11.1	0.4	32.8	1.2

Tables 3 and 4 show the recovery of minerals by wet and magnetic separation from the sediment samples, respectively. The amount of minerals in sediment is not uniform through out. Different locations give different concentration of minerals. The percent recovery of wet separation is not consistent for all locations. Sediment show heavy minerals content is high in zircon, followed by ilminite and monozite.

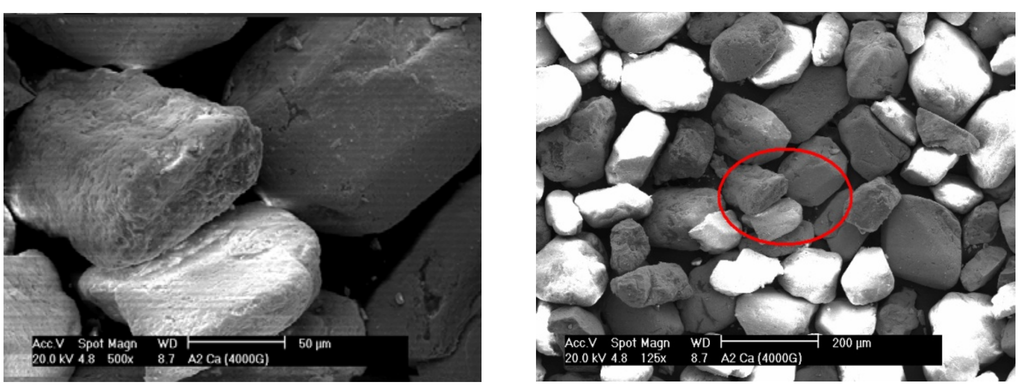
Table 3: Recovery of minerals from sediment containing ’amang’ by wet gravity separation as percentage of raw sample as percentage of raw sample

samples	mass (g)	wet separation (g)	percent recovery (%)
E1	600	80	13.3
E2	800	380	47.5
E3	410	none	None
E4	300	200	66.7
E5	200	none	none
E6	480	290	60.4
E7	350	200	57.1
E8	600	69	11.5
E9	600	28	4.7
E10	490	300	61.2
E11	850	none	none
E12	410	114	27.8
E13	550	54	9.8
E14	900	290	32.2
E15	590	320	54.2
E16	505	none	None
E17	210	199	94.8
E18	890	110	12.4
E19	300	210	70.0
E20	500	133	26.6

Table 4: Recovery of minerals from sediment by magnetic separation as percentage of raw sample

Sample(s)	monazite (g)	Recovery (%)	ilmenite (g)	Recovery (%)	Zircon (g)	recovery (%)
E1	0.3	0.1	0.3	0.1	66.8	11.1
E2	3.2	0.4	29.3	3.7	258.4	32.3
E3	none	none	none	none	none	none
E4	1.6	0.5	13.0	4.3	100.6	33.5
E5	none	none	none	none	none	none
E6	1.3	0.3	7.6	1.6	118.4	24.7
E7	3.7	1.1	7.4	2.1	120.6	34.5
E8	1.4	0.2	2.5	0.4	39.5	6.6
E9	1.1	0.2	3.9	0.7	15.4	2.6
E10	5.3	1.1	30.4	6.2	212.5	43.4
E11	none	none	none	none	none	none
E12	0.8	0.2	11.1	2.7	87.2	21.3
E13	1.9	0.4	4.6	0.8	37.1	6.8
E14	1.0	0.1	25.8	2.9	170.3	18.9
E15	17.2	2.9	88.1	14.9	123.1	20.9
E16	none	none	none	none	none	none
E17	1.1	0.5	17.4	8.3	122.9	58.5
E18	0.7	0.1	9.1	1.0	62.4	7.0
E19	none	none	21.4	7.1	150.9	50.3
E20	1.8	0.4	13.9	2.8	91.7	18.3

Figures 1a and 1b show the SEM morphology for monazite minerals recovered from the soil and sediment samples. Figure 2 show the EDX spectrum of monazite which at the energies from 2.00 keV and 5.00 keV, show a very intense peak of P, Ce and Nd respectively, present which proved the grain to be monazite [13] and this is consistent with the elemental formula of monazite which is , ([Ce, La, Nd, Gd, Th] PO_4). At the energy of 3.00 keV, a peak of Th appear since the monazite is a thorium bearing phosphate mineral and is one of the principal sources of rare earth elements and thorium in the continental crust [11]. Table 5 list the elemental content in percent for monazite being analyzed.



(a) (b)

Figures 1a and 1b: The morphology of monozite at different magnification (500 x and 125 x)

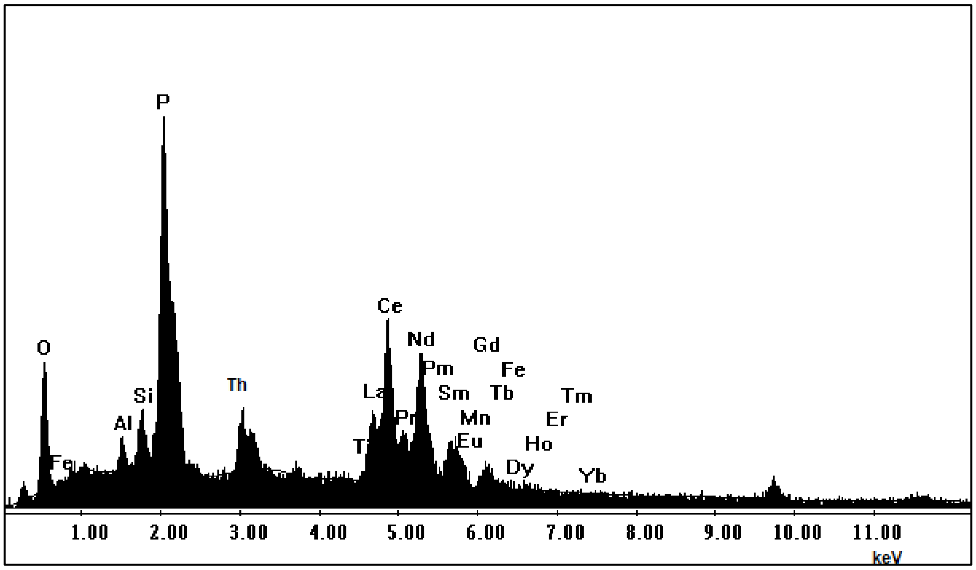
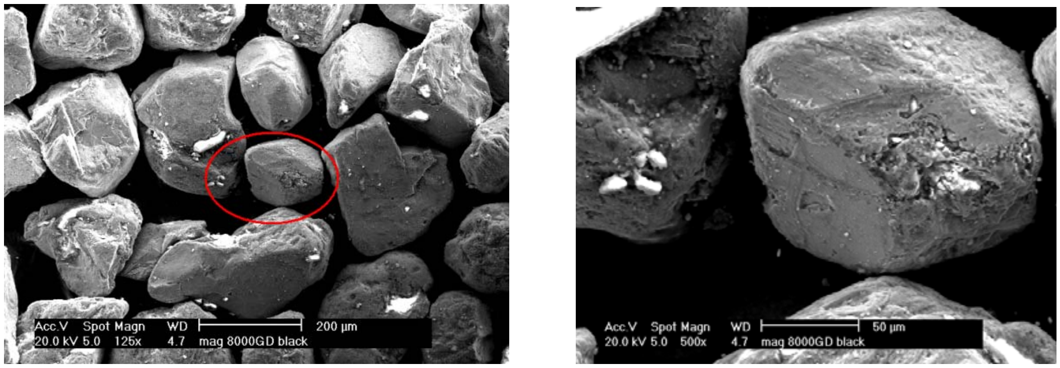


Figure 2: EDX spectrum of monozite recovered from soil and sediment samples

Table 5: Elemental composition of monozite recovered from soil and sediment samples

Element	**Wt %**	**At %**	**Element**	**Wt %**	**At %**
O K	9.04	31.42	PmL	1.54	0.58
AlK	1.77	3.64	SmL	2.55	0.94
SiK	3.01	5.96	EuL	2.65	0.97
P K	17.48	31.37	GdL	1.14	0.40
AgL	5.84	3.01	TbL	0.78	0.27
LaL	11.70	4.68	FeK	0.12	0.12
CeL	28.28	11.22	HoL	0.45	0.15
PrL	3.31	1.31	TmL	0.68	0.22
NdL	9.65	3.72	**Total**	**100**	**100**

Figures 3a and 3b show the morphology of ilmenite minerals from soil and sediment samples measured by SEM. Figure 4, show the EDX spectrum of ilminite which shows at the energy 4.50 keV, a very intense peak of Ti and at the energy of 6.50 keV, a peak of Fe appear together with some amount of Mn exist in these samples which confirmed it is ilmenite. This is consistent with data reported by Reyneke and Van Der Westhuizen [3] that ilmenite in its pure form is $FeTiO_3$, but also often contains some Mg and Mn, so that the formula would be fully expressed as (Fe, Mg, Mn)TiO_3. Moreover, the colour of the minerals is shiny black [3].



(a) (b)

Figures 3a and 3b: The morphology of ilminite at different magnification (500x and 125x)

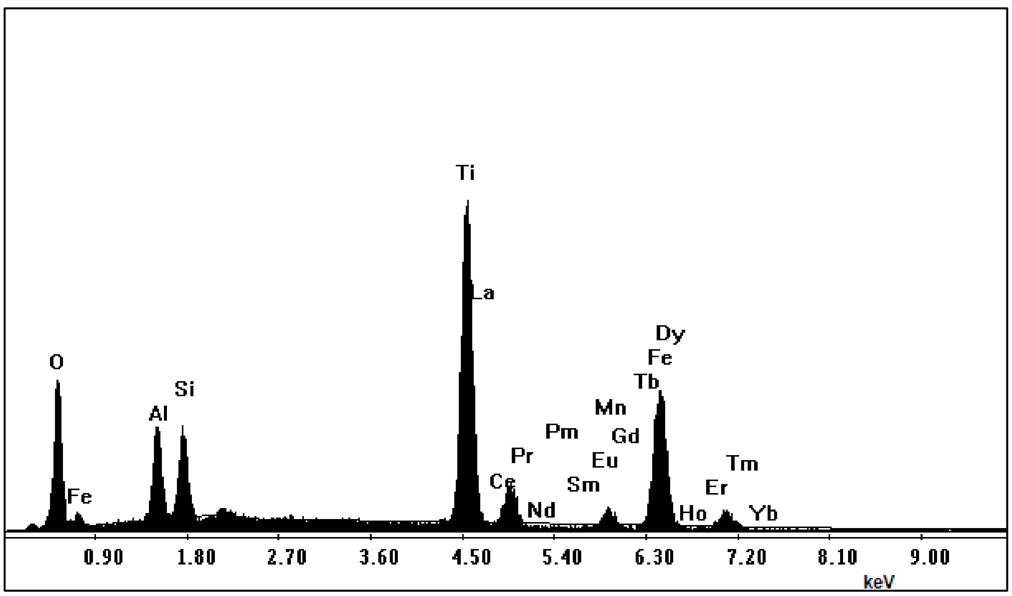
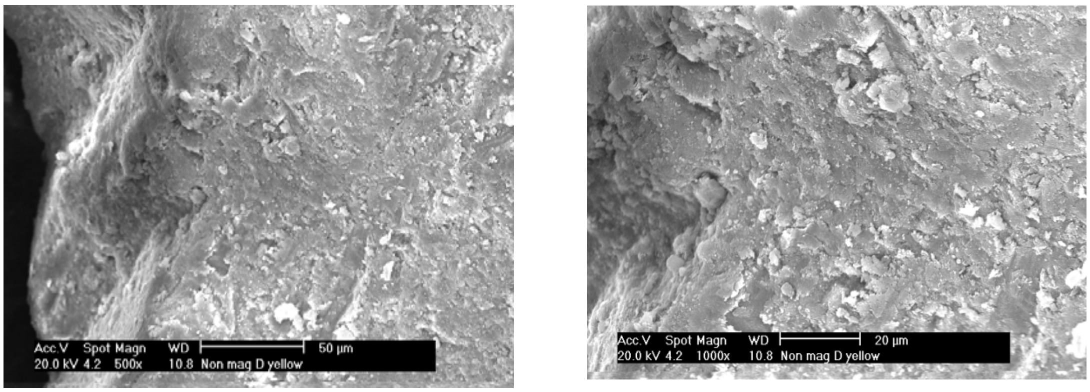


Figure 4: EDX spectrum of ilminite recovered from soil and sediment samples

Table 6: Elemental composition of ilminite recovered from soil and sediment samples

Element	**Wt %**	**At %**
O K	20.77	47.34
AlK	6.19	8.37
SiK	5.12	6.64
TiK	25.16	19.15
LaL	6.33	1.66
MnK	1.83	1.21
FeK	18.35	11.98
DyL	16.26	3.65
Total	**100**	**100**

Figure 6 shows the morphology of zircon minerals in the soil and sediment samples measured by SEM. Figure 7 shows the EDX spectrum of zircon. The Si peak appears at about 2.00 keV which is the major constituent of zircon as shown in the elemental formula of Zircon ($ZrSiO_4$). At the energy about 6.00 keV, a minor peak for Fe supported the grain to be zircon, however with some impurities of other elements like Mn and Ti [1, 14]. Furthermore zircon is a non magnetic mineral, another property of zircon [3, 10].



(a) (b)

Figures 5a and 5b: The morphology of ilminite at different magnification (500x and 125x)

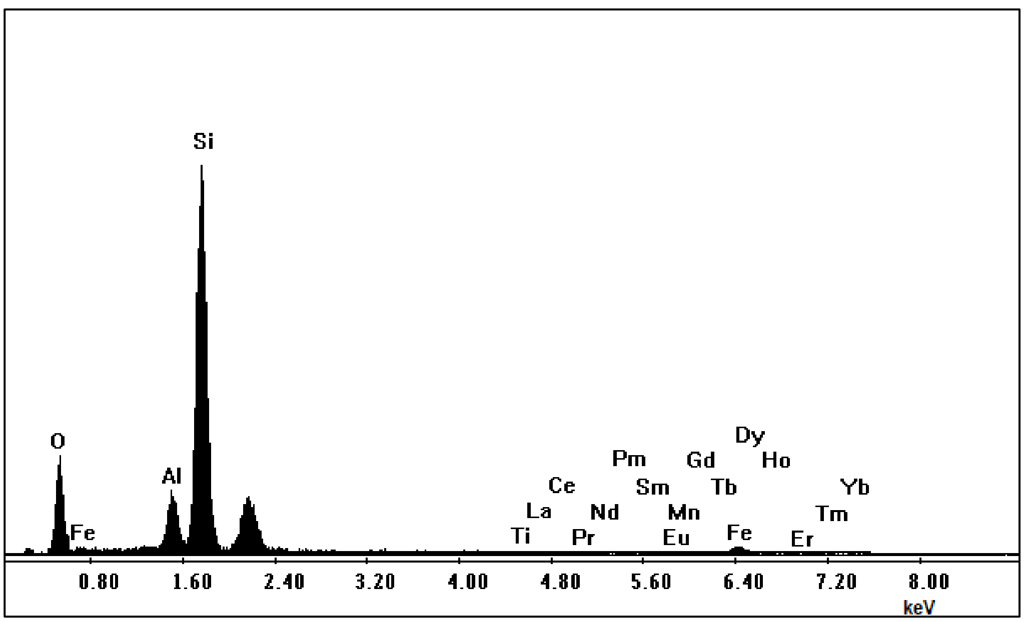


Figure 6: EDX spectrum showing the elemental composition of heavy minerals zircon.

Table 7: Elemental composition of zircon recovered from soil and sediment samples

Element	**Wt %**	**At %**
O K	30.90	45.79
AlK	7.90	6.94
SiK	53.34	45.02
TiK	0.14	0.07
FeK	3.83	1.63
DyL	1.97	0.29
TmL	0.61	0.09
YbL	1.31	0.18
Total	**100**	**100**

Table 8 shows the rare earth elements content in mg/kg measured in soil and sediment samples analyzed using ICP-OES. The results show the minerals (monazite, ilmenite and zircon) are containing rare earth elements which agree with the characteristic of individual minerals. In general one can conclude that monozite contains more rare earth elements compared to other heavy minerals like ilminite and zircon. These heavy minerals are the source of rare earth elements, but to extract these rare earth, one need to deal with the natural radionuclides such as uranium and thorium which are also present in heavy minerals.

Table 8: Concentration of rare earth elements (mg/kg) in soil and sediment samples

Minerals	**Samples**	**Sc**	**La**	**Gd**	**Lu**	**Dy**
monazite	A21(soil)	60.75	none	913.72	8.73	562.20
ilmenite	A21(soil)	48.47	none	501.92	9.14	342.66
zircon	A21(soil)	13.04	104.51	10.75	4.57	31.46
monazite	E10 (sediment)	21.27	526.54	47.70	4.61	66.07
ilmenite	E10 (sediment)	26.38	82.91	9.89	6.67	38.05
zircon	E10 (sediment)	12.23	45.91	7.61	3.90	7.10

Conclusion

From this study, one can conclude that soil and sediment samples from ex-mining area may contain heavy minerals like monazite, ilminite and zircon. They can be separated using wet separation method followed by magnetic separation. The SEM/EDX analysis on the minerals confirmed that the minerals are monazite, ilminite and zircon. Their rare earth elemental content were analyzed using ICP-OES and the results further support that heavy minerals are rich in rare earth elements.

Acknowledgement

Authors would like to thank Ministry of Science, Technology and Innovation (MOSTI) for the Grant 03-01-01-sf0084.

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