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Advances and Applications in Geospatial Technology and Earth Resources

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Contents

Distribution and Reserve Potential of Titanium-Zirconium Heavy Minerals in Quang an Area, Thua Thien Hue Province, Vietnam

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Abstract. Quang An, Thua Thien Hue province, Vietnam, is one of the areas with great heavy-mineral potential. The heavy-mineral ore body distributes along the beach with the width of 300–800 m and the length of about 6,100 m. A total of 4,398 samples were collected vertically in a grid pattern from 585 bore holes covering an area of 2.882 km^2. The results indicate that the ore body is in marine-eolian sediments at Late Holocene (mvQ_2^{2-3}). Useful heavy minerals were ilmenite, rutile, leucoxene, anatase, zircon and monazite which could be found in the intrusive and other rocks in the region. The total heavy minerals (THM) content in the bulk samples is not so high with average of 1.172%. The heavy mineral grains are small with the size of 0.05–0.25 mm and they are well liberated, rounded to sub-rounded. The average thickness of ore body is about 8.3 m, however, its variation is relatively stable with the coefficient of 39.28%. The average content of TiO_2 in ilmenites of 58.02% and ZiO_2 in zircons of 60.89% indicate that titanium-zirconium heavy minerals in Quang An area have relatively good quality. The proven reserves of total heavy minerals in study area were determined reliably with about 406.595 thousand tons, of which the measured mineral reserve is 68.177 thousand tons and the indicated mineral reserve is 338.418 thousand tons. This paper deals with the distribution and potential of heavy minerals in the study area in order to promote efficient mineral exploitation and mineral processing.

Keywords: Heavy minerals · Ilmenite · Zircon · Distribution · Reserve potential

1 Introduction

Beach-placer deposits are accumulations of heavy, resistant minerals with high specific gravity that form on upper regions of beaches or in long-shore bars in a marginal-marine environment. They form by mechanical concentration of heavy minerals by the action of waves, currents, and winds [6]. They typically consist of titanite, zircon, magnetite, ilmenite, monazite, apatite, rutile, xenotime, garnet, and

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allanite, among other minerals. Titanium-zirconium placer deposits have been exploited and served in various industries in many countries around the world like USA, Canada, Africa, Brazil, India, China [2–8, 12, 16]. Many studies on distribution, characteristics of heavy minerals in beach placer deposits around the world have been published [2–8, 12, 16]. Tyler and Minnitt pointed out the importance of the titanium-zircon heavy minerals and new business opportunities in the exploitation of these minerals in in South Africa [16]. Distribution, mineralogy and chemistry of heavy minerals in some placer deposits in India had been studied by Acharya et al. [2–5]. Based on detailed mapping and exploration drilling of some Late Cretaceous heavy mineral deposits in San Juan Basin, New Mexico, USA, McLemore fully evaluated resource and economic potential for these deposits in current changing economic market [12]. Recent years, many studies related to marine environmental geochemistry, marine sedimentary as well as heavy mineral placer deposits in Vietnam have been interested by scientist and investing companies [9–11, 13–15]. Existing survey reports indicate that there is great potential for total heavy mineral deposits along the coast of the country with high potential of titanium - zirconium heavy minerals. In the surveying report on potential of heavy minerals along coastal line from Thanh Hoa to Thua Thien Hue, it indicated that this region has a significant potential of heavy minerals and it should be studied systematically [9].

Quang An, Thua Thien Hue province, is one of the areas with great heavy-mineral potential in Vietnam (Fig. 1A). However, studies on heavy minerals in detailed for providing important data to investors are still limited. The aim of this paper is to discuss about the quality, spatial distribution characteristics of ore placer minerals and clarifies titanium-zirconium heavy minerals potential in Quang An area, in order to providing the necessary information for efficient exploration, exploitation, use of the resource.

2 Geological Features of the Study Area and Surrounding Region

2.1 Stratigraphy

Middle Cambrian - early Ocdovician A Vuong Formation ($\in_2$-O_1 av) is the oldest metamorphic unit in the region. It is exposed in the west of the study area as a range following a northwest - southeast orientation. Younger metamorphic unit is Late Ocdovician - Early Silurian Long Dai Formation (O_3-S_1 ld) which is exposed as a large area in the central region. The metamorphosed rocks comprise mostly shale, chert, tuffaceous sandstone, sandstone (Long Dai Formation) and quartz-feldspathic schist, quart-mica schist (A Vuong Formation). In the region, sedimentary rocks include Tan Lam (D_1 tl), A Lin (P_2 al), A Ngo (J_1 an) Formations which are exposed as scattered units in the region and alternated with other rocks (Fig. 1B). Compositions of these formations are mainly sandstone, musdstone, limestone [9].

The exploration results indicate that the study area presents two types of unconsolidated sediments with different origins (Fig. 2). Marine-eolian sediments at Late Holocene (mvQ_2^{2-3}) cover the whole study area with sand strips and dunes. The sediments

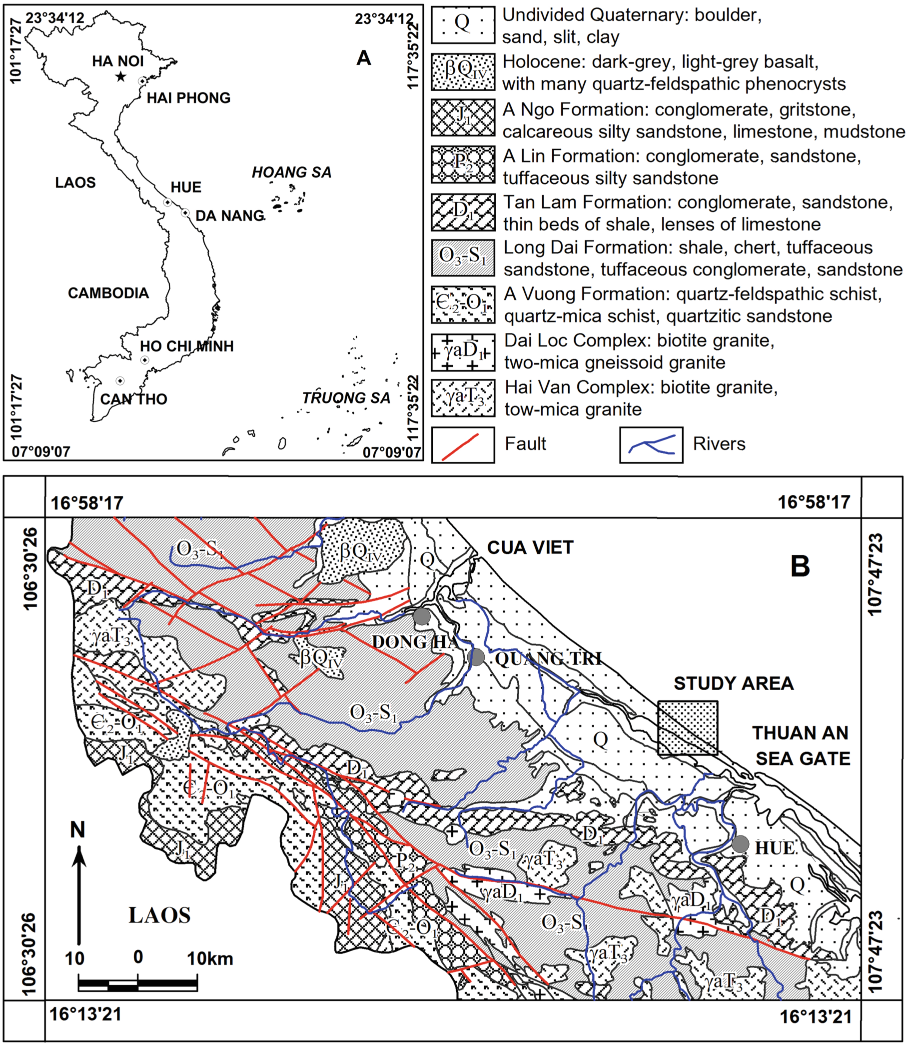

Fig. 1. Location of the study area in Vietnam (A); regional geological map (B)

comprise of small to medium-sized dark yellow, brownish-yellow quartz sand showing yellowish-gray color in the surface, containing many black heavy minerals. The average thickness of this layer is 8.3 m. Late Holocene fluvio-marine sediments (amQ_2^3) distribute along the western coast and are usually affected by sea waves, tides and river from the Tam Giang lagoon. The fluvio-marine sediments comprise of clay, clayey sand, sand containing less titanium-zircon minerals with thickness of 3–10 m.

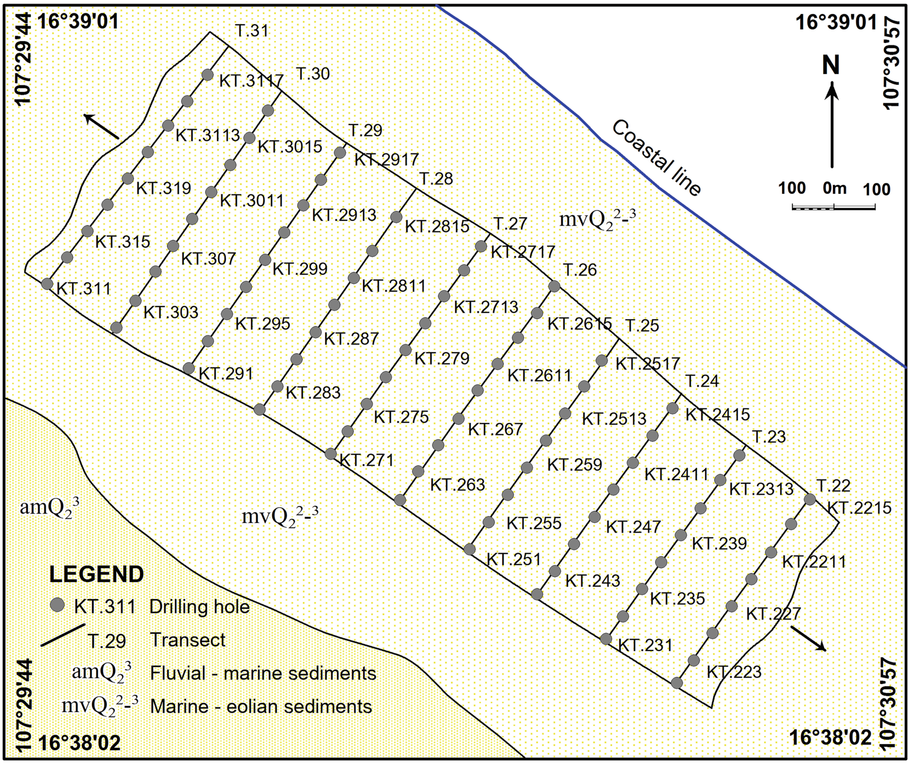

Fig. 2. Representive grid pattern of sampling in the study area

2.2 Magmatism

There is no intrusive rocks exposed in the Quang An study area. However, Dai Loc and Hai Van Complexes can be found in the surrounding areas (Fig. 1B). The rocks expose as small to medium bodies scattering in the western and southern parts of the region. These complexes consist mainly of biotite granite and two-mica granite. Containing a significant content of heavy minerals, these rocks were referred as important sources of the heavy minerals to the study area.

3 Methodology

3.1 Grid Pattern of Sampling

Samples were collected according to the regulations for the classification of reserves and resources of solid minerals of Minister of Natural Resources and Environment of Vietnam. Drilling grid patterns were defined with grids of 100 m × 20 m and 100 m × 40 m for the measured mineral reserve (121) and the indicated mineral reserve (122), respectively (Fig. 2) [1]. Fifty exploration transects with striking N35°E were set up to be perpendicular to the coast line in the study area. The 585 boreholes were drilled by hand augur drilling method. The bore depths were from 3.0 m to 16.0 m depending on the specific positions and ensure to cut through the thickness of the ore body. Each drilling interval of 0.5–1.0 m was taken one sample and the total number of collected sample is 4398. Drilling and sampling methods were described in detailed by Nguyen et al., 2011 [15].

3.2 Sample Preparation and Analysis

All samples were brought to the laboratory, dried and thoroughly mixed. The samples were then sieved with ASTM sieve numbering 16 (Size of 1.18 mm). Each sample was reduced to 20–30 g by coning and quartering processes. The samples were treated with water to remove the ultra fine clays. The dried sample was put in a heavy liquid Bromoform to separate to heavy and light minerals and the total heavy mineral concentration was calculated. Three groups of magnetic, electromagnetic and non-electromagnetic minerals were separated by using handling magnets. The heavy mineral fractions were taken to prepare the slides for the study under the microscope. The number percent of each of the heavy minerals was multiplied with their respective specific gravity values and the wt% of the individual member was calculated.

The heavy minerals were characterized using various techniques. The distribution of heavy minerals was determined by manual grain counting using an optical microscope (Leica-Wild M8). The morphological properties and mineral chemistry of heavy minerals were examined by using the scanning electron microscope (SEM - Quanta 450) with energy dispersive X-ray spectroscopy (EDS). X-ray powder diffraction patterns of the heavy mineral samples with different conditions were also measured using a D5005 S model powder diffractometer with Cu-Kα radiation at 40 kV and 30 mA, scanned from 3 to 70° at a goniometer rate of $2\theta = 2°\text{min}^{-1}$. The chemical composition of the samples was determined using X-ray fluorescence (XRF, Philips X Unique2).

3.3 Statistical Analysis

The content of heavy minerals are presented by descriptive statistics (mean, standard deviation (SD), minimum and maximum concentrations, skewness, variation coefficient etc.) using the SPSS Statistics software for Windows (SPSS Inc., Chicago, IL, USA, 2007). Together with standard deviation, coefficient of variation (CV), which is SD/mean, was used to reflect the degree of discrete distribution of different metal element concentrations and to indicate indirectly the activeness of selected element in examined environment.

The Spearman's rank correlation was used to examine the correlation between minerals. The correlation coefficient matrix measures how well the variance of each constituent can be explained by relationship with each other.

3.4 Reserve Calculation

The reserve of total heavy minerals in the study area is calculated by the geological block method. The equation is as follow: Q = S. M.C.D. Where: Q: Reserves of total heavy minerals (ilmenite + rutile + anatase + leucoxene + monazite + zircon, thousand tons. S: Square, thousand m^2. M: Average thickness of the ore body in the block, m. C: Content of THM, %. D: Weight of ore sand (ton/m^3).

4 Results

4.1 Mineralogy

Analysis results of heavy mineral samples indicate that there is almost no presence of magnetic minerals. Electromagnetic group includes mainly ilmenite, tourmaline, amphibole, sphene limonite, granate, epidote, monazite and so on. Heavy non-electromagnetic group consists of mainly zircon, less rutile, sillimanite, anatase, leucoxene. Among the above-mentioned minerals, useful ones in ore placers are ilmenite, zircon, rutile, anatase, leucoxene and monazite. SEM images indicate that the main heavy mineral grains are well liberated, rounded to sub-rounded (Fig. 3).

Statistic results show that the contents of total heavy minerals in deposits of the study area vary considerably with the average of 1.172%. The variation of ore mineral contents are uneven with a coefficient of variation of 49.0–87.4%. Useful heavy minerals correlate quite closely with a coefficient of correlation from 0.27 to 0.91 (Table 1).

Table 1. Pearson's correlation matrix for the useful heavy minerals in study area [16]

Minerals	Ilmenite	Anatase	Rutile	Leucoxene	Zircon	Monazite
Ilmenite	1.0					
Anatase	0.78	1.0				
Rutile	0.76	0.91	1.0			
Leucoxene	0.51	0.27	0.29	1.0		
Zircon	0.79	0.80	0.75	0.52	1.0	
Monazite	0.86	0.77	0.74	0.34	0.70	1.0

4.2 Grain Size Distribution

The heavy mineral distribution in different size fractions in bulk sample and after processing is given in Table 2 and Fig. 4.

Table 2. Grain size distribution of heavy minerals in the study area

Size fractions (mm)	Bulk (%)	Heavy minerals distribution after processing (%)			
		Ilimenite	Zircon	Rutile	Monazite
>0.5	0.33	0.0	0.0	0.0	0.0
0.50 ÷ 0.25	77.33	0.67	0.0	0.70	0.0
0.25 ÷ 0.10	20.18	48.07	4.05	63.30	1.15
<0.10	2.16	51.27	95.50	36.00	98.85

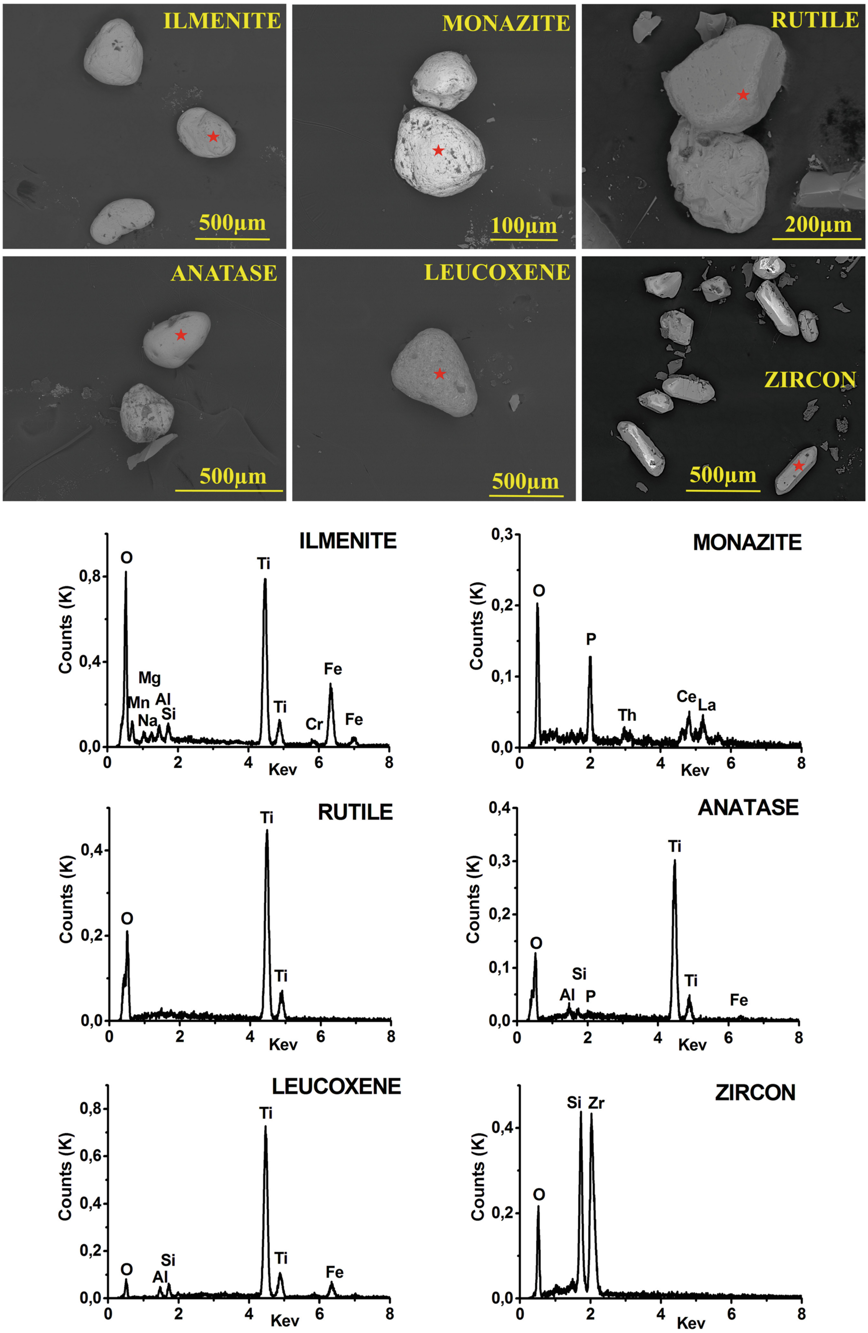

Fig. 3. SEM-EDS images of main heavy minerals in the study area

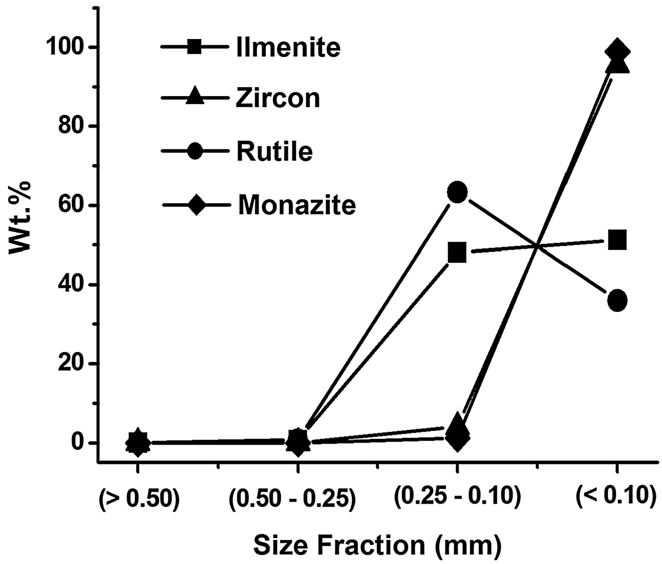

Fig. 4. Heavy mineral distribution after processing in different sieve fractions

Grain-size analysis shows that the bulk samples contain mainly small to medium and fairly uniform grains. Sand particles in the range of 0.1–0.5 mm account for about 97.51%. Minerals with size fraction above 0.5 mm are negligible with an average of 0.33%. Those with size fraction of less than 0.1 mm has a low percentage with an average of 2.16%. However, analysis results of concentrating ore indicate that concentrating ores of ilmenite, rutile, zircon and monazite contain small-sized particles mainly in the range of 0.25–0.05 mm. Ilmenite and rutile in the size of 0.5–0.25 mm are insignificant. Monazite and zircon grains are finer in size. The presence of heavy minerals above 0.25 mm is negligible.

4.3 Mineral Chemistry

Chemical analysis of bulk samples indicates that TiO_2 content ranges from 0.40% to 1.33%, average of 0.88%. ZrO_2 content ranges from 0.09% to 0.29%, average of 0.18% (Table 3).

SEM-EDS was used to determine the semi-quantitative contents of the oxides in the major heavy minerals in the study area (Fig. 3, Table 4). *Ilmenite* grains contain 58.02% TiO_2, 37.33% FeO, 1.97% MnO, 0.08% MgO, 0.07% Al_2O_3, 0.43% SiO_2, 0.51% Cr_2O_3, 0.22% Cao, 0.21% Na_2O, 0.23% K_2O and 0.30% P_2O_5 in average. Ilmenite in the studied mine has higher titanium dioxide and smaller ferrous iron than ilmenite in other places [2–8, 12, 16]. The existence of Mn^{+2} and Mg^{+2} may be due to their replacement for Fe^{+2} in the ilmenite structure. *Rutile* contains 95.12% TiO_2, 0.81% FeO, 0.87% Al_2O_3, 0.55% SiO_2, 0,64% Cr_2O_3, 0.57% MnO with trace amounts of Na, Mg, K. *Leucoxene* contains 4.40% FeO, 80.44% TiO_2, 7.15% Al_2O_3, 6.55% SiO_2, 0.10% MgO and 1.35% P_2O_5. Leucoxene compared to ilmenite has higher

Table 3. Chemical analysis of bulk samples in the study area

Oxide	Content (%)		
	Minimum	Maximum	Average
SiO_2	94.82	97.34	95.95
TiO_2	0.40	1.33	0.88
CaO	0.02	0.13	0.09
MgO	0.04	0.11	0.08
ZrO_2	0.09	0.29	0.18
Al_2O_3	0.68	1.33	1.00
FeO	0.010	0.03	0.02
Fe_2O_3	0.45	1.07	0.73
Cr_2O_3	0.002	0.006	0.004
MnO	0.010	0.05	0.03
P_2O_5	0.030	0.090	0.053
V_2O_5	0.001	0.003	0.002
SO_3	0.18	0.29	0.22

amounts of Ti, Al, Si and lower amounts of Fe. The higher contents of Al_2O_3 and SiO_2 in leucoxene may due to external sources during the complex alteration process [6]. *Anatase* has 92.65% TiO_2, 0.97% Al_2O_3, 0.45% SiO_2, 0.38% P_2O_5, 0.32% MgO, 0.17% CaO, 0.79% Cr_2O_3, 0.78% MnO and 3.5% FeO. SEM-EDS confirms the presence of Zr, Si in zircon and La, Ce and Th in monazite (Fig. 3, Table 4).

Table 4. Chemical analysis of heavy minerals in the study area

Oxide	Content (%)					
	Ilmenite	Rutile	Leucoxene	Anatase	Monazite	Zircon
Na_2O	0.21	0.38	0.00	0.00	4.55	1.70
MgO	0.08	0.09	0.10	0.01	–	–
Al_2O_3	0.70	0.87	7.15	0.97	3.57	1.94
SiO_2	0.43	0.55	6.55	0.45	3.02	35.47
P_2O_5	0.30	0.44	1.35	0.38	35.03	–
K_2O	0.23	0.19	0.00	0.32	–	–
CaO	0.22	0.34	0.00	0.17	–	–
TiO_2	58.02	95.12	80.44	92.65	–	–
Cr_2O_3	0.51	0.64	0.00	0.79	–	–
MnO	1.97	0.57	0.00	0.78	–	–
FeO	37.33	0.81	4.40	3.50	3.47	–
ThO_2	–	–	–	–	6.08	–
La_2O_3	–	–	–	–	16.63	–
Ce_2O_3	–	–	–	–	27.64	–
ZrO_2	–	–	–	–	–	60.89

4.4 Variation of Ore Body Thickness

Titanium-zirconium ore placer body lies horizontally, exposes on the terrain surface and spreads over the entire study area. Sand layer containing ore consists mainly of small to medium-sized grains which are dark yellow, yellowish-gray to light yellow in color. The results of hand drilling and sample analysis indicate that orebody thickness varies from 2.0 m to 15.0 m with the average thickness of 8.3 m. The orebody is relatively stable in thickness with the coefficient of variation of 39.28%. In parallel with the coastline, the thickness of orebody is less variable and tends to gradually decrease from north to south. As perpendicular to the coastline, the thickness of orebody appears to decrease from center to edge (Fig. 5).

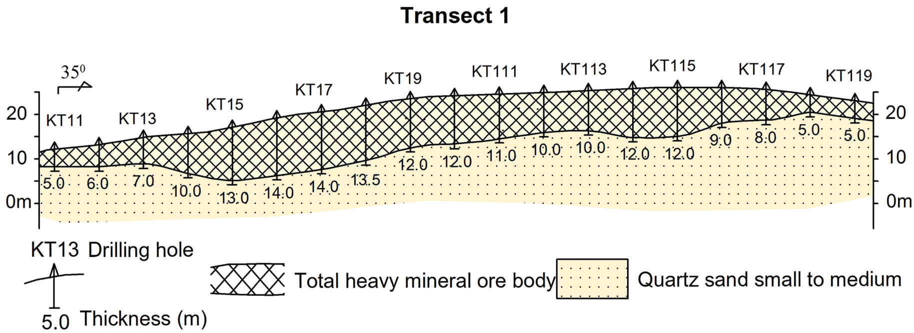

Fig. 5. Variation of orebody thickness in a representative transect 1

4.5 Distribution of Total Heavy Minerals

Research results show that valuable minerals in coastal placer at Quang Ngan area are mainly consist of ilmenite and less zircon, rutile, leucoxence, anatase and monazite. In general, the total heavy mineral contents considerably vary from low to medium grade with value of 0.251% to 3.35%, and the average of 1.17%. The total heavy mineral content varies unevenly with the coefficient of variation of 49.0%.

The results indicate that placer mineral contents vary considerably. These minerals also show quite clear distribution pattern. In general, mineral contents highly vary along the coast and perpendicular to the coastline. In parrallel with the coastline, heavy mineral contents tend to gradually decrease from center to northwest and southeast.

As perpendicular to the coastline, the contents of the total heavy minerals and heavy minerals normally appear to decrease from the continent to the sea. However, within the study area, this trend slightly changes with rich ores concentrating in the center in the form of strips and decreasing toward the two sides (Fig. 6). With depth, the results of hand drilling, sampling and sample analysis indicate that total heavy minerals are mainly distributed at the depth of 0–15 m with a cut-off of 0.25% THM (Fig. 6).

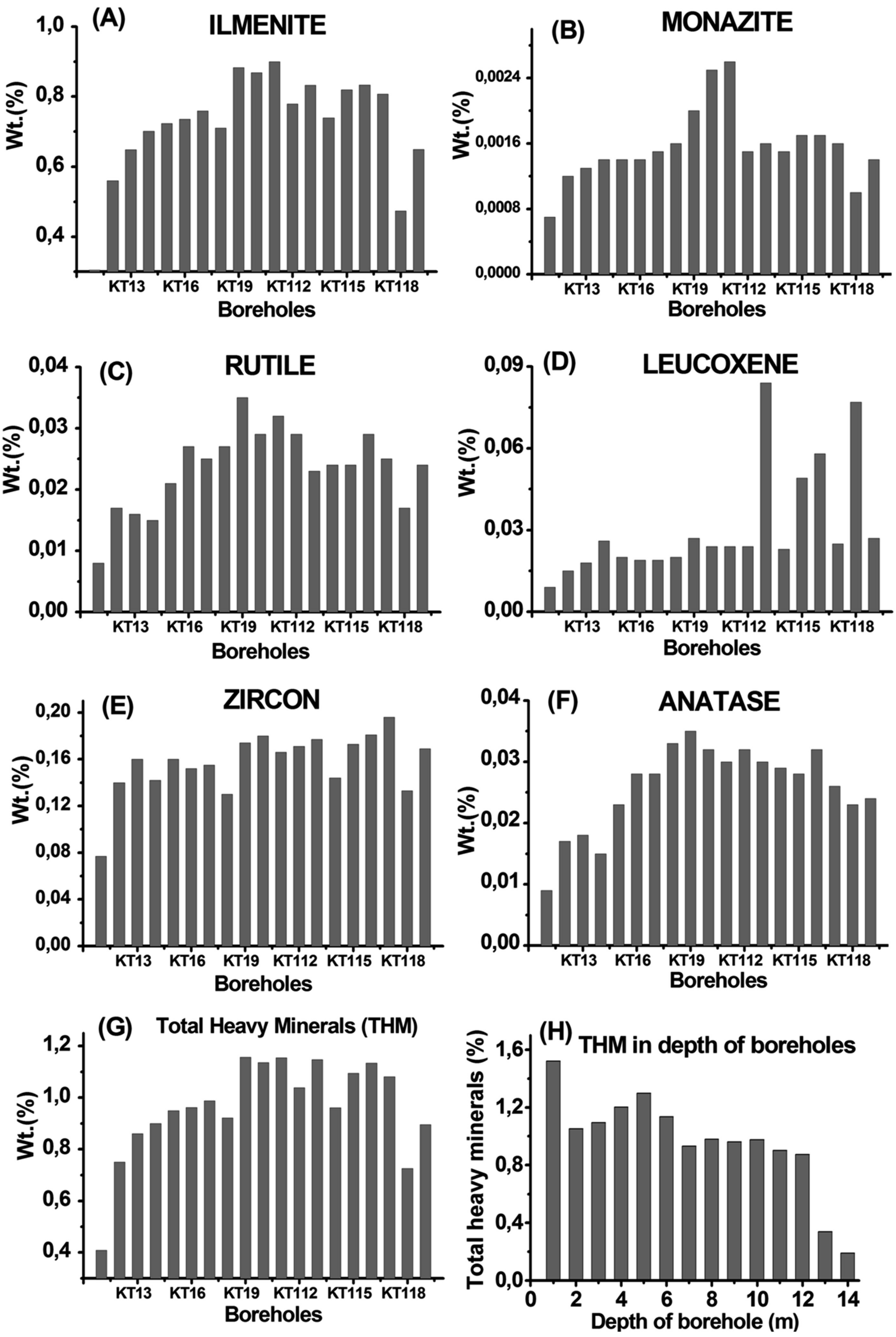

Fig. 6. Distribution of total heavy minerals in a representative transect 01

4.6 Reserve of Heavy Minerals

The parameters were selected for calculating the measured and indicated reserves of total heavy mineral in the study area including: a cut-off of 0.25% total heavy minerals in single sample and 0.50% in the block. The minimum thickness of the ore body is 1.0 m. The maximum thickness of waste sand is also 1.0 m.

Because the ore body in the study area is horizontal and its thickness is quite stable. All drilling holes were cut through the thickness of the ore body. Therefore, the method using to calculate reserves of total heavy minerals is the geological block method. Bourdary of block is connected by drilling grid patterns of 100 m × 20 m and 200 m × 40 m for level 121 (the measured mineral reserve) and 122 (the indicated mineral reserve), respectively (Fig. 2). The study area is divided into seven blocks (one block of level 121 and 6 blocks of level 122) and the proven reserves are shown in Table 5.

Table 5. Proven reserves of total heavy minerals in Quang an area

Block	Square (m^2)	Thickness (m)	Content of THM (%)	Dry weight (ton/m^3)	Proven reserve (1000 tons)
1–121	404700	9.19	1.207	1.52	68.177
Level 121					***68.177***
1–122	330000	9.51	1.328	1.52	63.301
2–122	392300	7.06	1.209	1.52	50.855
3–122	378900	6.60	1.109	1.52	42.116
4–122	431700	7.72	1.215	1.52	61.447
5–122	504100	7.81	1.139	1.52	64.092
6–122	432400	7.96	1.083	1.52	56.607
Level 122					***338.418***
Sum (121 + 122)					***406.595***

The calculated results indicated that the proven reserves of total heavy minerals in Quang An area, Thua Thien Hue province, Vietnam were about 406.595 thousand tons, of which the level 121 is 68.177 thousand tons and the level 122 is 338.418 thousand tons.

5 Discussion

Quang An is located in Quang Ngan and Quang Cong Communes, Quang Dien District, Thua Thien Hue Province, about 15 km to the north of Hue City (Fig. 1A). It is one of the areas with great heavy-mineral potential. The whole area is covered by marine-eolian sedimentary formations (mvQ_2^{2-3}) at Late Holocene (Fig. 1B). Mixed marine sediments form sand strips and dunes distributed on high elevation terrain with uneven surface. Typical components are small to medium-sized dark yellow, brownish-yellow quartz sand showing yellowish-gray color in the surface, containing many black heavy minerals. The heavy-mineral ore body is along the beach with the width of 300–800 m and the length of about 6,100 m. It has maximum thickness of 15 m, minimum thickness of 2 m and average thickness of 8.3 m. As perpendicular to the coastline, the thickness of orebody appears to decrease from center to edge because of sea waves and wind actions. Results indicate that the useful heavy minerals in the study area are mainly ilmenite, zircon, rutile, anatase, leucoxene and monazite. Close relationships between heavy minerals were referred to drive from the same source. Moreover, small and rounded to sub-rounded grains also indicate that these heavy minerals had been moved a long way along the rivers. The rivers in the region are important factors for carrying heavy minerals from the land to the beaches. After that, these heavy minerals had suffered from tectonic and neotectonic activities and other influences such as geomophology, sea waves, tides, winds and currents. In order to precisely identify the source rock and understand the depositional history of the placer deposit, detailed studies should be carried out.

In the bulk samples, the average total heavy minerals (THM), TiO_2 and ZrO_2 contents are 1.172%, 0.88% and 0.18%, respectively. These contents are not so high comparing with other coastal areas such as in Binh Thuan province [9–11]. The average content of TiO_2 in ilmenites of of 58.02% and ZiO_2 in zircons of 60.89% indicate that titanium-zirconium heavy minerals in Quang An area have relatively good quality. Heavy mineral grains in the Quang An area are small with mainly in the size of 0.05–0.25 mm. The average thickness of ore body is about 8.3 m, however, its variation is relatively stable with the coefficient of 39.28%. The proven reserves in Quang An area are determined reliably in accordance with the Regulations of Minister of Natural Resources and Environment of Vietnam with THM of about 406.595 thousand tons. This is important information for enterprises to invest in mining and processing heavy minerals in the study area.

6 Conclusion

- The results indicate that the ore body is in marine-eolian sediments at Late Holocene (mvQ_{23}) with an average ore body thickness of 8.3 m.
- Useful heavy minerals were ilmenite, rutile, leucoxene, anatase, zircon and monazite and grains are well liberated, rounded to sub-rounded. The average total heavy minerals (THM) content of the bulk samples is 1.172%.
- The ilmenites contain the average TiO_2 content of 58.02%. The zircons contain the average ZiO_2 content of 60.89%. Distribution of the total heavy minerals are mainly in the size of 0.05–0.25 mm.
- The proven reserves of total heavy minerals in study area were about 406.595 thousand tons, of which the level 121 is 68.177 thousand tons and the level 122 is 338.418 thousand tons.
- Although the distribution of grain size, orebody thickness, characteristic of mineralogy, mineral chemistry and mining conditions are relatively favorable for exploiting, environmental impacts should be carefully researched. High technology of mineral processing has to be selected to improve the content of heavy minerals effectively.

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