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Characterization of Radioactive and Rare Earth Elements in Heavy Minerals from River Sediments in Marau Region, Ketapang, West Kalimantan

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ABSTRACT

Alluvium deposits from the Kendawangan River located in Marau, Ketapang, West Kalimantan have been known for their radioactive and rare earth mineral potential. In this paper, heavy minerals taken from alluvium deposits will be characterized to determine the elemental distribution of uranium, thorium, and rare earth elements in each mineral and their mineralogical composition. The samples are taken by panning and prepared using the flotation method to obtain heavy mineral concentrates. Geochemical analysis was carried out using a Bruker M4 Tornado plus Micro-XRF and continued with mineralogical analysis using AMICS (Advanced Mineral Identification and Characterization System) software. It was found that the distribution of heavy minerals from the sand samples was dominated by manganoan ilmenite, ilmenite, rutile, zircon, magnetite, and monazite, as well as thorite, cassiterite, xenotime, allanite, and other minerals in small quantities. Uranium, thorium, and rare earth elements are found in monazite, thorite, xenotime, zircon, and allanite.

Keywords: heavy minerals, Micro-XRF, radioactive minerals, rare earth element

INTRODUCTION

Uranium and thorium are important strategic elements, they play a big role in nuclear power generation. In nature, uranium and thorium are commonly associated with rare earth elements, these elements are often found in the same mineral association and source rocks [1].

A radioactive mineral is a mineral that contains 0.05% (500 ppm) of radioactive elements [2]. Ketapang area and its surrounding, West Kalimantan is known to have potential for radioactive minerals such as monazite which usually contains thorium, uranium, and rare earth elements (Ce, La, and Nd). In general, this area is part of the Malay Penisulla-Sumatra-Kalimantan Granit Belt, which is known for its tin mining and potential for REE-bearing minerals such as monazite, xenotime, zircon, and apatite [3]–[5]. The result of radiometric mapping in the Ketapang Area shows that high radiometric anomalies are covered by granitic rocks and placer deposits near the granitic rocks [6], [7].

Based on previous research, ilmenite, zircon, and hematite are found as dominant heavy minerals in alluvium deposits [7]. Other heavy minerals identified are monazite, xenotime, thorite, magnetite, rutile, epidote, biotite, cassiterite, anatase, hornblende, tourmaline, sillimanite fluorite, and garnet [3], [7]–[10]. Monazite, zircon, and xenotime usually contain radioactive elements. The source of these radioactive minerals found in the alluvium deposit in this area likely came from Sukadana Granite [3], [6], [7], [9]–[12].

Geochemical characterization of rocks and minerals is very important to determine the potential of minerals and can be used as basic data for selecting processing methods. Usually, to characterize the bulk geochemistry of the rocks, X-ray fluorescence (XRF) is frequently employed. However, to obtain high spatial resolution trace element data, researchers often need to depend on laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) or synchrotron radiation X-ray micro-beam XRF (SR-μXRF) that need to be conducted in special facilities.

Benefiting from the latest advancements in X-ray optics, the development of laboratory-based, benchtop micro x-ray fluorescence (μXRF) gives researchers another resource to get clear and illustrate element distribution and semi-quantitative geochemical analysis, including trace elements analysis. Using this instrument, the elemental compositions across the surface area analyzed may be measured and reported as single points, lines, and maps. With this ability, micro XRF has the means to be an important tool for geochemical data collection, even though this instrument does not yet have the sensitivity and resolution of SR-μXRF [13]–[15].

This study aims to identify the distribution of uranium, thorium, and rare earth elements in heavy mineral grains and characterize uranium, thorium, and rare earth elements bearing minerals from river sediments in Marau, Ketapang, West Kalimantan. The research area is located in Marau District, Ketapang Regency, West Kalimantan. This area is part of the Kendawangan River watershed (Figure 1). Based on the regional geological map of Kendawangan Regency and its surroundings [16], the survey area is composed of six formations, from oldest to youngest: Pinoh Metamorphic Formation, Ketapang Formation, Sukadana Granite, Kerabai Volcanic Formation, Swamp Deposit, and Alluvium Deposit.

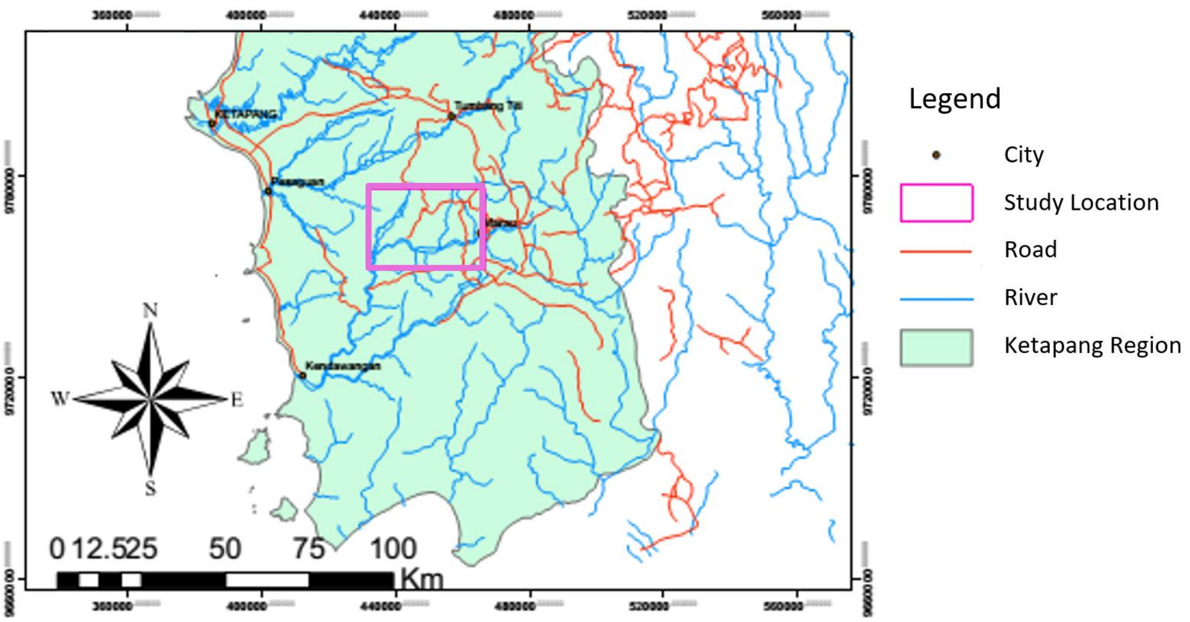

Figure 1. Map of research location

METHODOLOGY

The methodology used in this research is geochemical and mineralogical analysis. Geochemical analysis was carried out using the Bruker M4 Tornado Plus Micro-XRF tool, followed by mineralogical analysis done using AMICS (Advanced Mineral Identification and Characterization System) software.

Geochemical analysis using Bruker M4 Tornado plus Micro-XRF tool was carried out to collect element distribution map data from selected samples. This element map can also be quantified to obtain pseudo-bulk composition values. Analysis was carried out on four heavy mineral samples that had been glued to the surface of the glass slide. The four samples are heavy mineral samples from panning that have been prepared to leave heavy mineral concentrates. Epoxy, polishing, or carbon coating are not needed in sample preparation, thereby speeding up the analysis process. The Micro XRF instrument operates in area mode with a vacuum of 20 mbar, voltage and current of 50 kV and 600 µA, X-ray size of 20 µm, acquisition time of 15 ms/pixel, and pixel size of 25 µm. Further analysis was carried out using AMICS software from Bruker Nano Analytics to identify minerals in the analyzed area. Mineral identification is carried out by comparing the spectrum of each pixel with the database contained in the AMICS software.

RESULTS AND DISCUSSION

The content of uranium, thorium, and rare earth elements in heavy mineral sample grains was detected using a micro XRF instrument. By using area scan mode, we can get the distribution map of the elements in the sample, in which we can see in which grains the uranium, thorium, and rare earth elements are distributed (Figure 2). Furthermore, the small size X-ray beam of micro XRF allows the retrieval of spectrum data on individual mineral grains. This spectrum data can be converted to the element concentration of the individual grain.

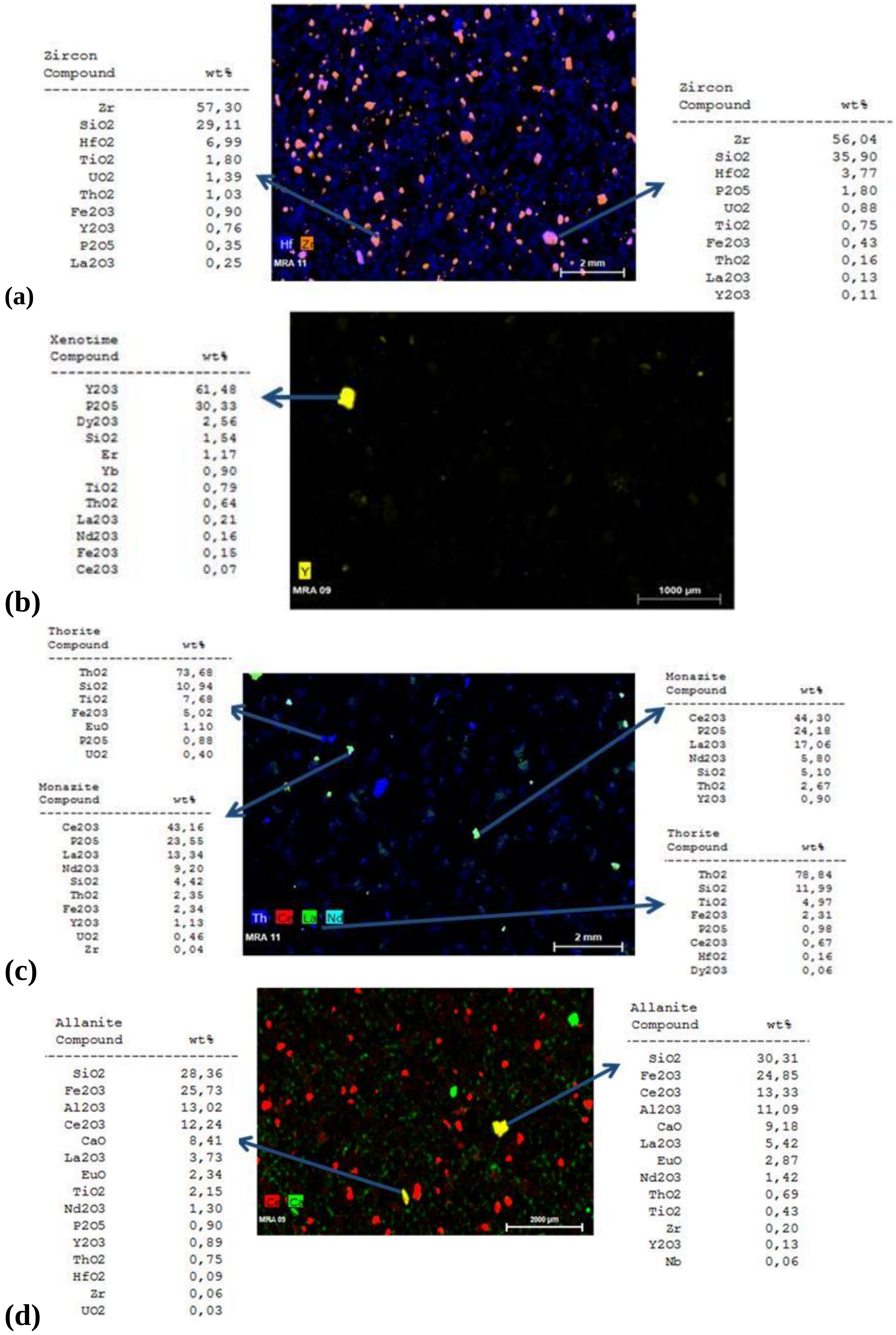

Figure 2. The spatial distribution of radioactive and rare earth elements of selected mineral grains through Micro XRF analysis at (a) zircon, (b) thorite and monazite, (c) xenotime, (d) allanite

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The results of a geochemical analysis from the micro XRF Bruker M4 tornado tool were thus further analyzed using AMICS software to determine the overall mineralogical composition, the result can be seen in Figure 3, Table 1, and Figure 4.

Ilmenite is considered the primary mineral source of titanium. Ilmenite has the formula (Fe, Mg, Mn)$^{2+}$ TiO_3. Ilmenite grains are dominated by black to reddish black. Based on the results of Micro XRF analysis in the selected grains of the ilmenite the TiO_2 content ranged from 49.4–72.5 wt% and Fe_2O_3 22–48.5 wt%, apart from that the elements MnO (<5 wt%) and Nb (<0.3 wt%) were also detected in the ilmenite grains.

Manganoan ilmenite was found to be the most dominant mineral of the four samples analyzed. This mineral is a variation of ilmenite with a fairly high Mn content. The formula of manganoan ilmenite is $(Fe,Mn)^{2+}TiO_3$. Manganoan ilmenite grains are predominantly black. The chemical composition of manganoan ilmenite obtained from the selected grains is TiO_2 49.3–56.8 wt%, Fe_2O_3 21.1–27.1 wt%, MnO 13–20 wt%.

Rutile is the second most abundant mineral found in the heavy mineral concentrate samples analyzed. Rutile grains are dominated by dark red to pink in color. The major element composition in several selected rutile grains showed TiO_2 concentrations reaching 92–99 wt%, other elements detected included Fe_2O_3.

Magnetite has the formula $Fe^{2+}Fe^{3+}{}_2O_4$. Magnetite mineral grains show a black to brownish-black color. The brownish color can be caused by the alteration/weathering/oxide processes that occur. The major element composition of the selected magnetite grains showed a Fe_2O_3 content of 93–99 wt% with other elements detected including SiO_2, TiO2, Al_2O_3, and CaO.

Cassiterite has the chemical formula SnO_2. In the samples, this mineral was found in small quantities. The major element composition of the selected cassiterite grains showed a Sn content of 48.6–66 wt%, SiO_2 25.3–38.5 wt% with other elements detected including TiO_2, Fe_2O_3, and Zr.

Zircon ($ZrSiO_4$) is an accessory mineral commonly found in nature. Zircon can be found in a variety of sedimentary, igneous, and metamorphic rocks. Zircon was found in the four samples studied at high levels. The major element composition of the selected zircon grains shows a Zr content of 63.6–77.8 wt%, SiO_2 17–28.2 wt%, Hf 0.7–1.5 wt%, some samples also show the presence of the elements Th, U, Ce, and La.

Monazite is generally radioactive due to its thorium and uranium content. Cerium is the most common REE obtained from monazite. Monazite mineral was found in all samples analyzed. Most of the monazite is white (Figure 5a). Based on the analysis of major and trace elements in selected grains, the monazite in the sample has a composition of Ce_2O_3 43–1.6 wt%, P_2O_5 15–27.4 wt%, La_2O_3 12.6–18.7 wt%, Nd_2O_3 6.2–13.7 wt%, ThO_2 1.2–4.6 wt%, and also the element U in low amounts.

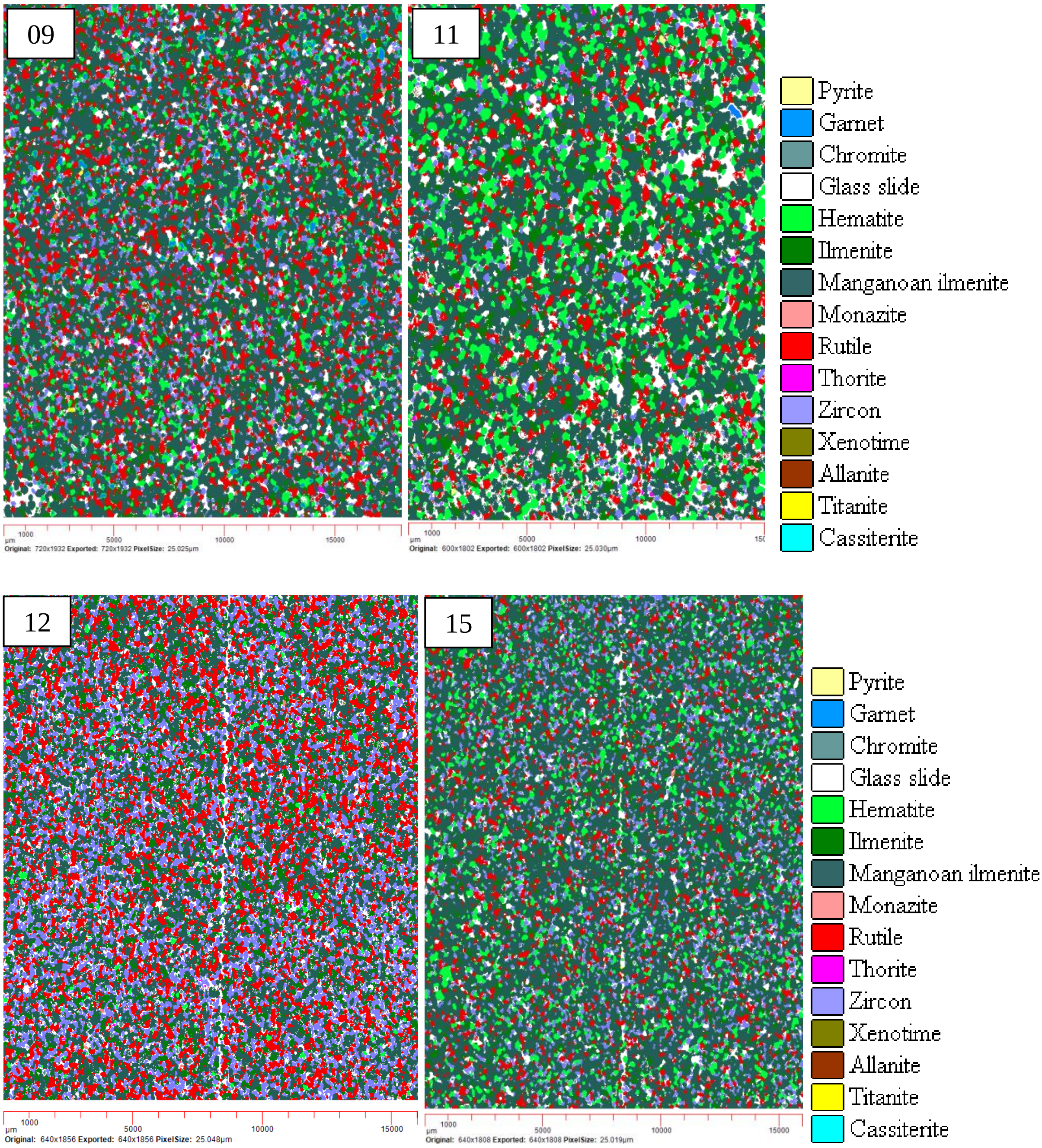

Figure 3. Mineral Mapping results for samples 09, 11, 12, and 15

Thorite has the chemical formula (Th, U)SiO_4 and can also contain rare earth elements. Thorite is commonly found as accessory minerals in acidic igneous rocks and also as detrital minerals in sediments. Thorite was detected in all samples analyzed, most of the thorite grains had a red color (Figure 5b), with the chemical composition of selected grains being ThO_2 72.8–81.4 wt%, SiO_2 7.64–12 wt%, UO_2 0.02–1.12 wt%, some grains also showed REE content such as Ce, La, Dy, and Nd.

Xenotime, having the formula YPO_4 is commonly found as an accessory mineral in alkaline to granitic igneous rocks and is a common mineral in placers. Xenotime was found in small quantities in three samples. Based on xenotime analysis, several selected grains have a composition of Y_2O_3 47.92–61.48 wt%, P_2O_5 14.8–30.33 wt%, Dy_2O_3 1.3–5.68 wt%, Er 0.44–1.17 wt%, and other minor elements detected include Th, La, Nd, and Ce.

Allanite is a member of the epidote group minerals, and has the chemical formula $Ca,(REE)^{3+}Al_2Fe^{2+}[Si_2O_7][SiO_4]O(OH)$. It is an accessory mineral in granite, pegmatite, and syenite, and is also found in metamorphic rocks and clastic components in sedimentary rocks. Allanite was found in minor amounts in the two samples studied, with the composition of selected grains SiO_2 28.36–30.31 wt%, Fe_2O_3 24.85–25.73 wt%, Al_2O_3 11.09–13.02 wt%, Ce_2O_3 12.24–13.33 wt%, CaO 8.41–9.18 wt%, La_2O_3 3.33–5.42 wt%, and other minor elements such as Th, U, Nd, Ti.

Table 1. Mineralogical composition of heavy mineral concentrate

Name	9	11	12	15
	wt %			
Allanite	0.02	0.01	0	0
Chromite	0.02	0.03	0.34	0.14
Magnetite	8.45	19.83	1.08	9.92
Ilmenite	8.79	11.5	12.08	11.31
Manganoan ilmenite	53.66	53.58	39.89	55.7
Monazite	0.75	0.2	0.26	0.16
Rutile	17.31	11.15	24.92	9.96
Thorite	0.72	0.22	0.15	0.07
Xenotime	0.02	0	0.01	0.01
Zircon	9.12	3.27	21.2	12.71
Other minerals	1.16	0.2	0.06	0.02

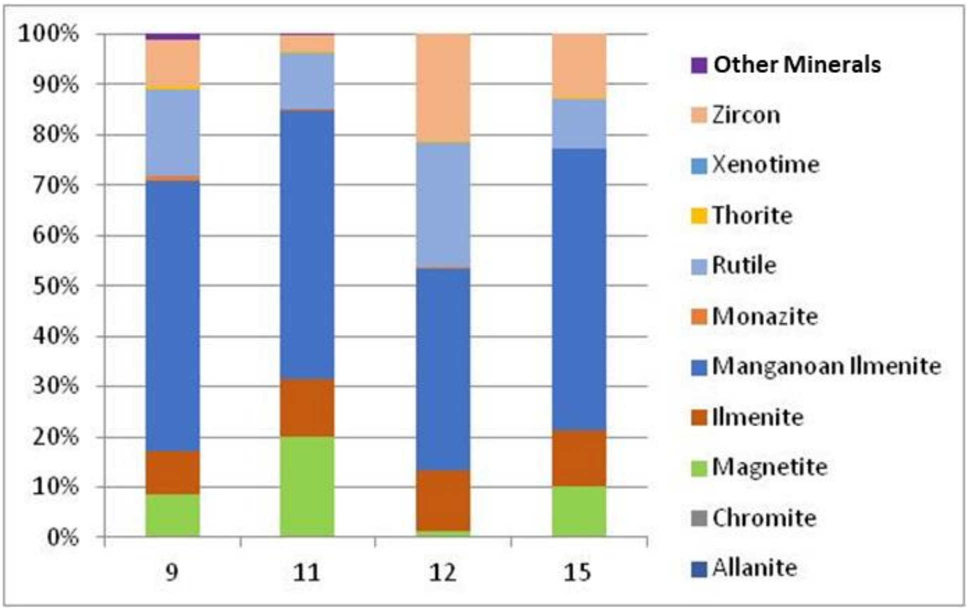

Figure 4. Proportion of minerals in heavy mineral concentrate

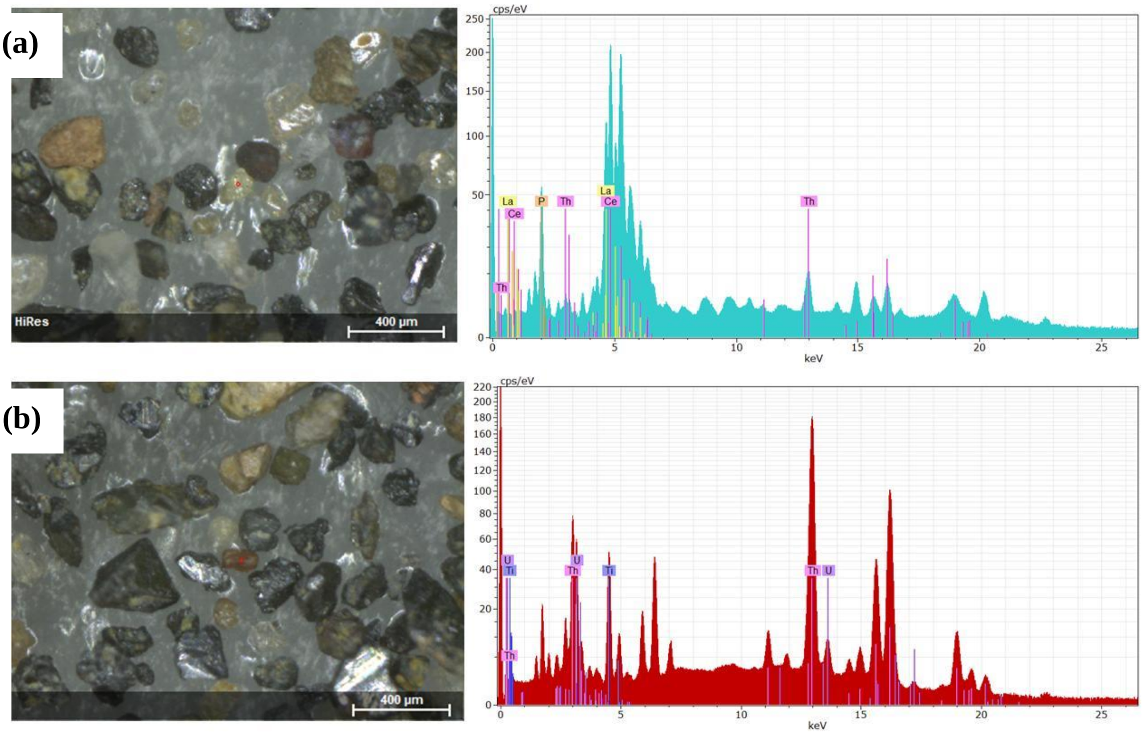

Figure 5. Micro XRF result of selected (a) monazite grain (b) thorite grain

Distribution of radioactive elements and rare earth metals

The presence of elements such as cerium, lanthanum, neodymium, thorium, and sometimes uranium is detected in monazite grains. Apart from monazite, high levels of cerium and lanthanum elements were also detected in the allanite mineral. High levels of thorium, up to 81 wt%, were detected in the thorite grains. Thorium and uranium were also detected in the zircon mineral. Yttrium and HREE elements such as Dy and Er are found in xenotime grains. Monazite, thorite, xenotime, zircon, and allanite can be classified as radioactive elements and rare earth metals bearing minerals in the research area.

In nature, mostly rare earth phosphates appear as monazite and xenotime. Monazite tends to bind large and light rare earth elements (LREE), while xenotime is more likely to bind smaller and heavier rare earth elements (HREE) [17]. In the sample studied, monazite was assessed as the main mineral carrying LREE (Ce, La, and Nd), apart from that, LREE enrichment was also detected in the mineral allanite. However, the presence of allanite in the sample is scanty, so the presence of LREE in allanite was assessed as insignificant. Xenotime as an HREE carrier mineral (Dy and Er) is found in small amounts in the sample, so the HREE enrichment in the sample did not appear significant.

The zircon intensity in the analyzed samples is quite high, especially in sample 11, where the zircon content reaches 21%. Zircon is known to contain many minor and trace elements and contains U and Th elements [18]. Analysis of selected grains shows that zircon contains the elements Hf, U, Th, and also REE, such as Ce and La. Even though the REE element content in zircon is lower than in monazite and allanite, the predominant presence of zircon makes this mineral quite attractive as a source of REE in the research area.

CONCLUSION

Characterization of radioactive and rare earth elements in heavy minerals is very important to determine the potential and can be used as basic data to determine the processing method. Micro XRF method allows rapid and simple geochemical analysis of thousands of heavy mineral grains in a matter of hours. The small spot of the micro XRF beam allows analysis of a single mineral grain so that the composition of each mineral grain can be figured. With the addition of AMICS software, the mineralogical composition can also be identified. Elemental mapping from Micro XRF shows radioactive and REE are distributed in specific grains, thus we can accurately determine the radioactive and REE-bearing minerals from the heavy mineral samples. Radioactive and rare earth bearing minerals identified in river sediments from the Kendawangan watershed are monazite, thorite, xenotime, zircon, and allanite. Other heavy minerals identified are manganoan ilmenite, ilmenite, rutile, hematite, cassiterite, chromite, garnet, magnetite, manganosit, and pyrite.

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