

## Platinum group mineral identification in river sediments along the tributaries of Sungai Kapuakan, Ranau

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**Abstract:** Platinum (Pt), palladium (Pd), iridium (Ir), ruthenium (Ru), rhodium (Rh), and osmium (Os) are known as platinum group elements (PGE). Their unique physical and chemical properties contribute heavily to sectors that regulate and develop the modern world. Recognizing the importance of this commodity, a study on the heavy minerals in Sungai Kapuakan, Ranau was conducted to evaluate the occurrences of minerals containing platinum group elements. The occurrences of minerals containing PGE are usually associated with ultrabasic host rock, such as peridotite, which are distributed in several areas within the island of Borneo. Previously, a report discussing the heavy minerals within the area of Sungai Kapuakan, Ranau stated occurrences of platinum group minerals (PGM) in the main river and its tributaries. The accessibility of the study area prompts the initiative for a preliminary study regarding this commodity before exploring other remote areas in Borneo with potential. Through quantitative mineral estimation (QME) analysis on concentrate samples extracted from the area, the main heavy minerals identified were magnetite, chromite, monazite, leucoxene, zircon, rutile, and ilmenite. The mineral identified as PGM via QME was verified through x-ray diffraction (XRD) analysis as sperrylite, an opaque platinum arsenide mineral (PtAs<sub>2</sub>) commonly associated with ophiolitic placers. Another PGM detected by XRD analysis was laurite (RuS<sub>2</sub>). Based on the results obtained through QME, the minerals associated with PGM for the study area are magnetite (Fe<sub>3</sub>O<sub>4</sub>), chromite (FeCr<sub>2</sub>O<sub>4</sub>), monazite ([Ce,La,Nd,Th][PO]<sub>4</sub>), leucoxene (Fe<sub>2</sub>O<sub>3</sub>TiO<sub>2</sub>), rutile (TiO<sub>2</sub>) and zircon (ZrSiO<sub>4</sub>).

**Keywords:** Platinum group minerals, river sediments, heavy minerals, tributaries, quantitative mineral estimation, economic geology

### INTRODUCTION

Platinum group elements (PGE) or platinum group metals are a group of six elements; platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru), and osmium (Os). The unique physical, chemical, and mechanical properties of PGEs raise them among the most valuable metals in the world. These metals are essential in modern world industries. Contributions in sectors such as industrial, chemical, electrical, medical, pharmaceutical, dental, glass, and jewelry are what make PGEs crucial for the modern world. The world resource for PGE is estimated at a total of 100,000 tonnes with South Africa containing the largest reserve in the Bushveld Complex (Mineral Commodity Summaries 2022 by U.S. Geological Survey, 2022). The 2022 Mineral Commodity Summaries stated that in 2021 the prices of platinum, palladium, and ruthenium increased by 35%, 18%, and 88% respectively compared to 2020 while the others reached record highs as the estimated price for rhodium doubled and iridium more

than tripled. Recognizing the economic importance of these underexplored commodities, the Department of Minerals and Geoscience Malaysia as part of the 12<sup>th</sup> Malaysia Plan (RM Ke-12) conducted a study to investigate the potential of PGE resources in Sabah. The focus of this study is to validate the occurrences of platinum group minerals (PGM) commonly found within ophiolitic placers by recognizing the physical properties of minerals containing PGE as well as its associated minerals. This will be obtained through the quantitative mineral estimation (QME) method which will then be validated through X-ray diffraction (XRD). This study will establish the type and occurrences of platinum group minerals as well as their characteristics within the study area of Kapuakan, Ranau, Sabah.

### PLATINUM GROUP MINERALS

From the periodic table, platinum group elements are transition metals from the second (Ru, Rh, Pd) and third (Os, Ir, Pt) series. These transition metals can also be divided

into 'light' and 'heavy' with regard to their atomic mass and density. Chemically they are quite similar but they have quite a considerable difference physically. Platinum and palladium are soft and malleable (Czerczak *et al.*, 2012). They have high resistance to oxidation and high-temperature corrosion. Rhodium and iridium are harder. Chemical compounds with these two metals are essential in numerous alloy applications. Ruthenium and osmium are hard and brittle. Despite having poor oxidation resistance, they are valuable alloy additives and catalysts.

According to the International Mineral Association, there are 109 species of platinum group minerals recognized. They can be grouped into sulfides, tellurides, arsenides, antimonides, alloys, and native species. Naturally occurring minerals of PGE may contain all of the six elements with a pre-dominance to either platinum or palladium and various amounts of the others. Native platinum is never purely platinum as it forms natural alloys with platinum being the dominant metal (Bateman, 1950). PGEs are distinctively chalcophile and are mostly contained in base-metal sulfide minerals (e.g., chalcopyrite,  $\text{CuFeS}_2$ ) or PGE accessory minerals (Lorand *et al.*, 2008). PGEs in some platinum group minerals also bonded to a variety of ligands with S, As, Sb, Te, and Se (Brown, 2008).

PGE ores are generally grouped into three primary classes: PGE dominant ores, Ni-Cu dominant ores, and miscellaneous ores (Xiao & Laplante, 2004). PGE-dominant ores are primarily exploited for their PGE content with Cu, Ni, and Co associate minerals as by-products. This class is further divided into Merensky type, chromite type, placer type, and dunite pipes. Ni-Cu dominant ores contrast as PGEs are discovered as by-products. This class is further divided into four classes (class I to IV) depending on the region's igneous activity. The third primary class is termed miscellaneous ores which contain very low PGE concentration with little to no economic value. Here PGEs are considered accessory metals and in some cases are not even recovered as a by-product (Cole, 2011).

PGE deposits are always associated with Ni-Cu sulfides in magmatic rocks (Naldrett, 2004). Host rocks for these platinum group elements generally range from mafic to ultramafic igneous rocks such as peridotite, pyroxenite, and dunite (Birke *et al.*, 2018). Weathering and erosion of these PGE-bearing host rocks produce PGE-bearing placers. In Alluvial deposits, they are associated with chromite, magnetite, and ilmenite (Reimann & de Caritat, 1998).

## GEOLOGY OF STUDY AREA

The terrain of Sg. Kapuakan forms a dendritic drainage pattern in which sub-tributaries flow into tributaries that connect to the main river. The regional geology of Sungai Kapuakan generally consists of three formations (Chert-Spilite, Crocker, and Trusmadi formations), two igneous bodies (ultrabasic rocks and granodiorite) and a

quaternary deposit (Figure 1). Previously known as the Danau Formation, the term Chert-Spilite Formation was used by Fitch in 1955 (Fitch, 1955). It later became widely accepted in the stratigraphic nomenclature of Sabah due to the association of spilite, pillow basalt, and ribbon chert (Wilson, 1961; Adams & Kirk, 1962). Ribbon chert of Upper Valanginian to Barremian age represents a layer of the ophiolitic basement sequence while the pillow basalts and spilite represent another layer (Hutchison, 2005). A large portion of the study area is underlain by alternating thin to massive sandstone and shale from the Crocker Formation aging from Eocene to Oligocene (Keij, 1963; Muda, 1993). The grey-colored sandstones in the area are fine to medium-grained with a few coarse-grained. The shale is grey to dark grey and reddish.

Hutchison (2005) stated that the content of Trusmadi Formation is predominantly dark argillaceous rocks. Low-grade greenschist facies metamorphism produces slate and phyllite with moderate to strong deformation. The thickness of argillaceous beds reached up to 30 meters. The dark grey, commonly sheared and phyllitic argillaceous rocks' mineral content is normally quartz, muscovite, chlorite, opaque minerals, and some carbon. Quartz veining is a very distinguished characteristic of this formation (Jacobson, 1970). Spilite outcrops within the Trusmadi Formation suggest an oceanic crust deposition environment (Hutchison, 2005). Some limestone micro-breccias are enveloped in phyllites. Foraminifera that exists in limestone lenses indicates the formation's Paleocene to Middle Eocene age (Keij, 1963; Collenette, 1965).

The igneous bodies within the study area consist of ultrabasic rocks and granodiorite. Past petrography and geochemical study of the area concluded that the ultrabasic rocks from this region are peridotite, and dunite formed by a low K tholeiitic magmatic series in the mid-ocean ridge basalt environment (Umor & Mohamad, 2003). They were classified based on the volume of olivine content. In peridotite, olivine content covers around 40% to 80% of the rock's volume whereas dunite covers more than 90%. Peridotites in Ranau area can be further divided into lherzolite, harzburgite, and wehrlite based on their pyroxene content. Within the study area, Cretaceous to Early Tertiary ultrabasic rocks occur as small fault-bounded outliers containing serpentinite and harzburgite.

Quaternary conglomerate deposits also occur within the study area. These poorly sorted deposits contain angular ultrabasic clasts ranging from fine to boulder size. Recent alluvial deposits can also be observed along Sungai Kapuakan and several of its tributaries. The occurrence of harzburgite-type peridotite and the angular ultrabasic clasts of quaternary conglomerate deposits as possible host rocks of PGE minerals triggers the interest to initiate this study. Figure 1 shows the regional geology of Sungai Kapuakan, Ranau, and the location of panned concentrate sampling.



homogeneity. Gravimetric separation via bromoform was used to separate heavy minerals from light minerals. Dried heavy mineral samples then underwent another separation according to their magnetic properties. Strong magnetic minerals were taken out using a hand-magnet. The rest were then further segregated using a Frantz Isodynamic magnetic separator with an initial current value set at 0.4 mA. The process is repeated with the values of 0.7 mA and 1.0 mA as well. The remainder grains unattracted by 1.0 mA are labeled as non-magnetic minerals. Minerals that have been separated according to their current value were weighed to determine their weight percentages. Despite the quantitative approach of this method, qualitative observations were made to identify the optical properties of PGMs (Craig & Vaughan, 1994).

**X-ray diffraction sample preparation**

To verify the minerals identified via QME, X-ray diffraction (XRD), a well-known reliable and rapid method of obtaining qualitative mineralogical data (Pryor & Hester, 1969) was conducted on a few selected samples based on the QME occurrences of platinum group minerals and the amount of available panned concentrate samples. This method of analysis was defined as a non-destructive technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material (Titus *et al.*, 2019). The intensity of the diffracted rays scattered at different angles of material are plotted to display a diffraction pattern. Due to the material’s specific chemistry and atomic arrangement, each phase of the material produces a unique diffraction pattern. The diffraction pattern is a simple sum of diffraction patterns of each phase. Imperfections present in the sample material would affect the pattern of the diffracted signal. The factors that contribute to the imperfection of the sample would be the composition heterogeneity, crystal structure defects, microstains, and

crystallite size (Epp, 2016). From the pattern, the type and quantity of the crystalline phase of the material can be identified. The qualitative phase analysis of the diffraction pattern of XRD characterization will be compared with the International Center for Diffraction Data (ICDD), a standard crystallographic database that aids the phase identification of a material in a large variety of heavy minerals crystalline samples.

The sample preparation for XRD requires 10 g of mortar grinded panned concentrates. The samples were well ground to powder (<40 µm) to ensure that all planes of crystallites were detected thus increasing the favor of obtaining accurate intensity ratios and a good signal. The prepared samples were scanned using a 40kV, 40MA Panalytical Empyrean diffractometer at several angles from 2° to 90°. The minerals detected are then compared with the results obtained from QME to provide a more affirmative conclusion for this study.

**RESULTS AND DISCUSSION**

Table 1 shows the minerals identified for all twelve samples at different magnetic factions. Due to its high magnetic susceptibility, magnetite minerals (Fe<sub>3</sub>O<sub>4</sub>) were mostly extracted by hand magnet with a few quartz coated with magnetite. The presence of this black opaque rock-forming mineral indicates a basic to ultrabasic host rock. Chromite (FeCr<sub>2</sub>O<sub>4</sub>) which is an indicative associate mineral of PGM occurred in a wider range of magnetic factions. This black greasy metallic lustred mineral constituents in 0.4 mA and 0.7 mA for all samples and occurred in six samples for 1.0 mA magnetic faction. Monazite ([Ce,La,Nd,Th][PO<sub>4</sub>]) which displays a yellowish green colored monoclinic crystal system is present in all magnetic factions with the exception of hand magnet and the highest in 1.0 mA. Leucoxene (Fe<sub>2</sub>O<sub>3</sub>TiO<sub>2</sub>) was identified in eleven samples mostly within non-magnetic. Leucoxene is most probably an altered product and mixture of Fe-Ti oxides associated with ilmenite and hidroilmenite.

**Table 1:** Minerals identified at different magnetic factions and their number of occurrences.

Hand-magnet		0.4 mA		0.7 mA		1.0 mA		Non-magnetic	
Minerals	Samples occurred	Minerals	Samples occurred	Minerals	Samples occurred	Minerals	Samples occurred	Minerals	Samples occurred
magnetite	12	chromite	12	chromite	12	monazite	11	zircon	12
quartz	9	ilmenite	11	monazite	10	chromite	6	leucoxene	11
		monazite	9	hidroilmenite	8	leucoxene	6	rutile	11
		hematite	3	ilmenite	3	rutile	4	quartz	6
		garnet	3	hematite	3	hidroilmenite	4	monazite	3
				garnet	1	zircon	3	PGM	4
				amphibole	1	hematite	2	pyrite	1
				tourmaline	5	pyrite	1	staurolite	1
				iron ore	1	pyroxene	1	scheelite	1
				leucoxene	1	staurolite	1		

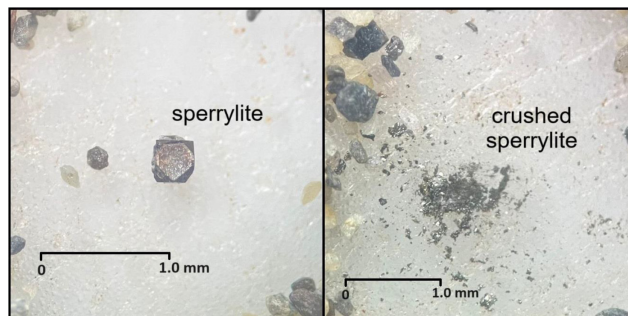
Another oxide mineral composed of  $TiO_2$  is rutile, a blood red colored adamantine lustered mineral mostly identified within non-magnetic. Zircon ( $ZrSiO_4$ ) exhibits clear to pinkish color, adamantine luster, and tetragonal crystal system. This mineral occurred in all samples within the non-magnetic fraction and a few within 1.0 mA.

Table 2 shows the mineral constituent percentage of each sample calculated from the fractions observed via QME. Quantitatively, the main heavy minerals identified were magnetite, chromite, monazite, and zircon. Magnetite and chromite were identified as the major constituents ranging from 1.99% to 67.16% for magnetite and 4.45% – 44.02% for chromite. Monazite and zircon were identified in all samples but constitute lower percentages ranging from 0.07% to 12.54% for monazite and 0.1% – 7.39% for zircon. The presence of non-heavy minerals such as quartz (4.83% to 34.16%) is highly influenced by the mineral’s tendency to be coated with magnetite. Ilmenite, leucoxene, and rutile can also be classified as part of the main minerals due to each being present in eleven out of twelve samples. Quantitatively, these titanium minerals range from 2.65% to 14.33% for ilmenite, 0.17% to 6.28% for leucoxene, and 0.18% to 4.36% for rutile. Hydroilmenite which ranges between 0.13% to 11.71% is a weathered evolution of ilmenite with reduced magnetism. Tourmaline which can be observed as a black-colored mineral with vitreous luster occurred within the range of 0.07% to 5.51%. Minerals such as garnet (0.94 – 4.95%) and hematite (0.91 – 2.07%) are classified as accessory minerals due to them being present in only three out of twelve concentrate samples. The same can be classified for minerals that only occurred in one sample such as scheelite (0.87% in sample RNUYC003), staurolite (3.44% in sample RNUYC008), pyroxene (0.08% in sample RNUYC010), amphibole (0.93% in sample RNUYC006), and pyrite (1.13% in sample RNUYC012).

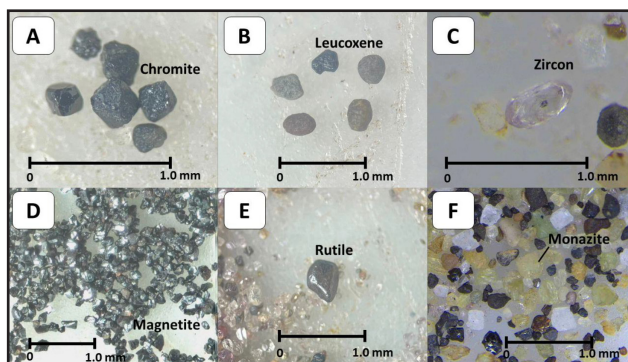
Minerals within the non-magnetic fraction were mainly focused on identifying and quantifying platinum grains as they are naturally paramagnetic (Albert & Rubin, 1971). Characteristics such as steel grey color, metallic luster, and malleability were used as references for identifying platinum grains. Malleability however is less prioritized as platinum group minerals containing ruthenium and osmium tend to be brittle (Birke *et al.*, 2018). No native platinum grains were identified. However, two types of minerals were taken into consideration claiming them to be platinum group minerals. The first is an opaque cuboctahedron mineral (Figure 2). When crushed, the brittle grain produces shattered metallic black fragments. Another possible species of PGM was presented as a black-colored opaque mineral with a metallic luster. These mineral grains spark curiosity as most black-colored minerals such as tourmaline, chromite, and ilmenite contain magnetic properties as demonstrated in Table 1. With the possibility of being a species of PGM, these mineral grains were speculatively labeled as PGM.

Four samples were identified containing PGM which are RNUYC001 (0.44%), RNUYC003 (0.17%), RNUYC004 (0.12%), and RNUYC007 (0.26%). Magnetite, chromite, rutile, leucoxene, monazite, and zircon can be classified as associate minerals of PGM as their occurrences can be observed in each sample containing PGM (Figure 3).

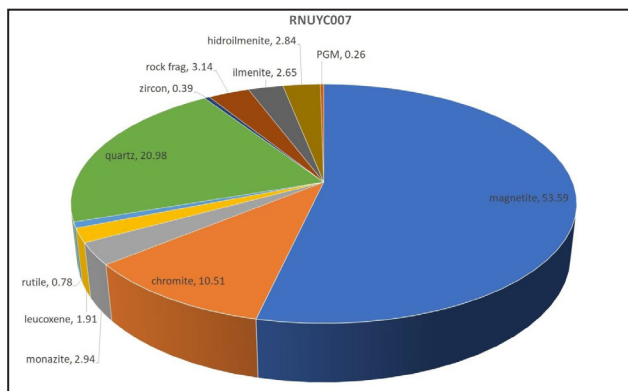
To verify the occurrences of PGM, XRD analysis was tested on an excess sample of RNUYC007. Figure 4 is a pie chart that illustrates the mineral constituents obtained



**Figure 2:** Olympus SZ61 stereo microscope view of cuboctahedron mineral grain identified generally as PGM (left). Microscopic view showing black metallic fragments of crushed PGM grains (right). Optically, the mineral grain showed properties of sperrylite.



**Figure 3:** Olympus SZ61 stereo microscope view showing the associate minerals for PGM; (A) chromite, (B) leucoxene, (C) zircon, (D) magnetite, (E) rutile, and (F) monazite.



**Figure 4:** Pie charts illustrating the quantitative mineral estimation of heavy mineral constituents for sample RNUYC007.

**Table 2:** Mineral constituent percentage calculated from the fractions observed via QME.

Sample	Mineral constituents (%)																				
	magnetite	chromite	monazite	leucosene	rutile	quartz	zircon	rock frag	ilmenite	hidroilmenite	tourmaline	garnet	iron oxide	scheelite	amphibole	staurolite	hematite	pyroxene	pyrite	PGM	
RNUYC001	59.96	16.67	12.54	0.27	0.18	7.7	0.44	1.13					0.67								0.44
RNUYC002	7.69	39.44	1.28	6.28	1.79	19.83	7.39		3.68	4.36	5.51	2.74									
RNUYC003	59.17	8.69	10.83	0.97	0.52	9.36	1.56		7.23		0.64			0.87							0.17
RNUYC004	59.41	13.13	10.94	0.84	0.47	4.83	1.52		8.55		0.2										0.12
RNUYC005	1.99	44.02	4.98	2.02	2.81	27.28	6.95	6.82	2.98	0.13											
RNUYC006	13.03	20.7	0.07	1.34	1.95	29.35	6.91	1.73	14.33	1.27	1.73	4.95	1.73		0.93						0.26
RNUYC007	53.59	10.51	2.94	1.91	0.78	20.98	0.39	3.14	2.65	2.84											
RNUYC008	60.4	13.83	0.72			10.94	0.47	1.71	4.03	4.46					3.44						
RNUYC009	61.05	6.24	2.5	0.31	0.21	15.59	0.1	2.1	3.85	6.42							1.63				
RNUYC010	54.78	4.45	1.92	0.4	1.74	20.84	0.4	5.12	4.68	3.51							2.07	0.08			
RNUYC011	67.16	6.21	0.91	0.17	4.36	8.53	0.34	1.03	3.72	6.64							0.91				
RNUYC012	10.09	17.95	3.94	0.34	3.18	34.16	2.43	3.7	10.36	11.71	0.07	0.94									1.13

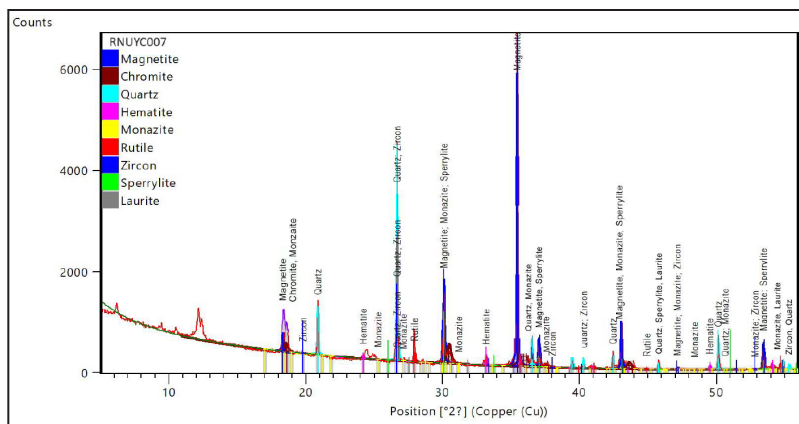


Figure 5: X-ray diffractogram showing minerals detected for sample RNUYC007.

via QME analysis for sample RNUYC007. Aside from the minerals identified via QME, the diffractogram for sample RNUYC007 (Figure 5) detected the presence of sperrylite. Sperrylite is a platinum arsenide mineral ( $PtAs_2$ ) commonly distributed in placers associated with ophiolitic peridotites (Cabri *et al.*, 2022). The detection of sperrylite verifies the cubic mineral identified generally as PGM via QME. QME analysis matches several descriptions of this mineral such as opaque transparency, cuboctahedron crystal system, brittle hardness, conchoidal fracture, and metallic luster (Castroviejo, 2023). Besides sperrylite, laurite which is another common PGM associated with ophiolitic placers was also detected from the diffractogram in Figure 5. Laurite is an opaque black sulfide mineral ( $RuS_2$ ) with a metallic luster. Laurite grains are difficult to identify via QME due to their visually similar characteristics as other dark minerals such as ilmenite, chromite, rutile, and tourmaline. However, this brittle sub-conchoidal mineral can be distinguished from the stated black minerals due to its non-magnetic properties (Malitch *et al.*, 2017). Hence, backed by the detection via XRD, laurite can be identified within the non-magnetic fraction. Figure 6 shows the microscopic image of two black-colored, metallic luster mineral grains with sub-conchoidal fractures identified as laurite.

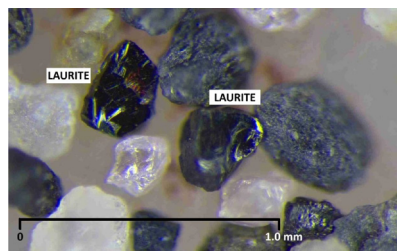


Figure 6: Olympus SZ61 stereo microscope view showing two black-colored, metallic luster minerals with sub-conchoidal fracture identified as laurite.

The main river which is the Sg Kapuakan flows from northwest to southeast. The dendritic drainage system of this area is strongly influenced by the topography of the land. The valley-like geomorphology of Sg Kapuakan causes its tributaries to flow towards the main river making them a possible route to trace the origins of PGE host rocks. Preliminarily, samples RNUYC006 and RNUYC009 were expected to yield PGM due to the proximity of the sampling point to the ultrabasic rock source. QME analysis results indicate the absence of PGM in both of these locations. This may be due to the lack of source rock erosion resulting in the absence of placers containing PGM. Based on the occurrences of PGM observed from the QME analysis of the concentrate samples, Figure 7

shows the possible migration pattern of PGM throughout the drainage system. The occurrences of PGM in samples RNUYC001, RNUYC003, and RNUYC004 might originate from the geological boundary of the ultrabasic body that contacts the river as shown in Figure 1. However, the low quantity of PGM observed via QME analysis might also suggest that they were transported from further upstream. This can also be supported by the rather rounded grains of PGM as well as its associated minerals. The absence of PGM in samples RNUYC002 and RNUYC005 shows that tributaries from the north might not be a possible pathway to trace the origin of PGE host rocks probably due to the extension of Crocker Formation sediments further up north. The occurrence of PGM in sample RNUYC007 suggests that the host rock might originate from the west. The absence of occurrence in sample RNUYC011 suggests that PGM transported along the sub-tributary did not make their way to Sg Pandiruan.

**CONCLUSION**

By conducting QME and XRD analysis, the PGMs detected were sperrylite and laurite. Through XRD, the PGM identified via QME was verified as sperrylite ( $PtAs_2$ ), an opaque metallic lustered platinum arsenide mineral commonly associated with ophiolitic peridotites. Backed by XRD, laurite ( $RuS_2$ ) was identified within the non-magnetic

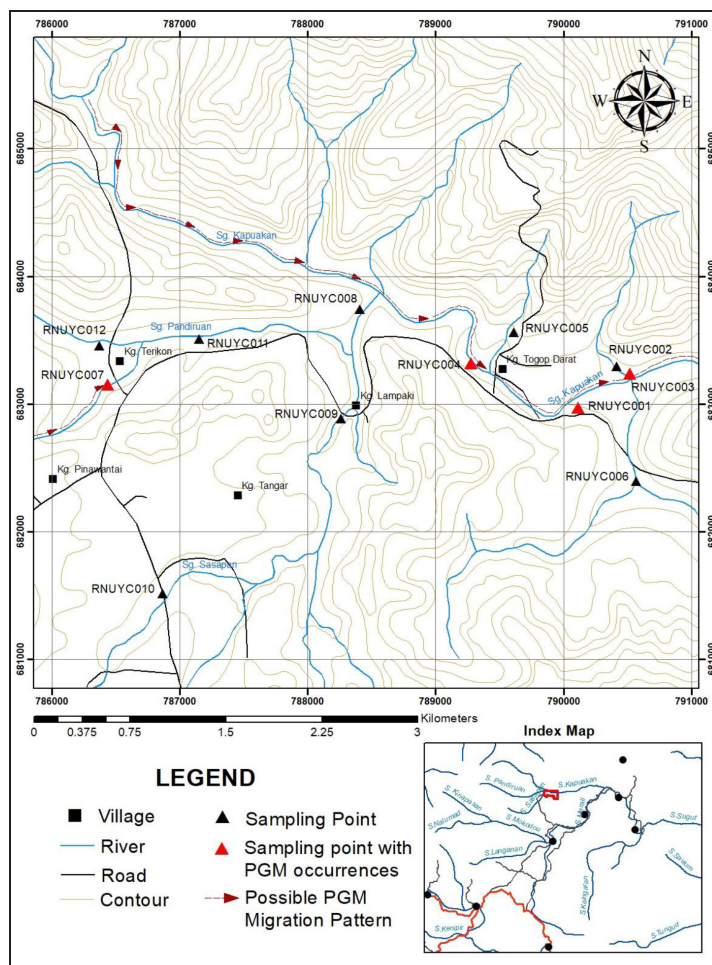


Figure 7: Map of Sg Kapuakan, Ranau showing sampling location with PGM occurrences as well as the possible migration pattern of PGM.

faction via QME. This black-colored opaque mineral is very brittle and has a sub-conchoidal fracture as well as a metallic luster. The occurrences of PGM were identified via QME in four sampling points namely RNUYC001, RNUYC003, RNUYC004, and RNUYC007. The tributaries of Sg Kapuakan flow towards the main river which flows eastward. The distribution of PGM occurrences suggests that the PGE host rock may originate from three sources; within the boundary of the ultrabasic igneous body, upstream of Sg Kapuakan or northwest of the study area, and west of the study area. The main heavy minerals identified in the tributaries of Sungai Kapuakan, Ranau were magnetite (1.99% to 67.16%), chromite (4.45% to 44.02%), monazite (0.07% to 12.54%), leucoxene (0.17% to 6.28%), zircon (0.1% to 7.39%), rutile (0.18% to 4.36%), and ilmenite (2.65% to 14.33%). The minerals associated with PGM are magnetite ( $Fe_3O_4$ ), chromite ( $FeCr_2O_4$ ), monazite ( $[Ce,La,Nd,Th][PO_4]$ ), leucoxene ( $Fe_2O_3TiO_2$ ), rutile ( $TiO_2$ ) and zircon ( $ZrSiO_4$ ). Through this simple study, the objective of verifying the presence of PGM was established. A more detailed study involving a detailed geological mapping and geochemical survey will be done to further understand this commodity thus providing vital information regarding its mineability.

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### AUTHORS CONTRIBUTION

MYK: Conceived and designed the analysis, collected field data, performed QME analysis, and wrote the paper. BM: Aid in designing the analysis and supervising the research paper. MSM: Contributed analysis tools and performed XRD analysis. JFSM: Contributed in fieldwork design and analysis tools.

### CONFLICT OF INTEREST STATEMENT

The authors whose names are listed certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript. The submission of this manuscript has been reviewed and approved by the officials within the Department of Mineral and Geosains Malaysia.

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