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Microchemical characterization and stream sediment composition of alluvial gold particles from the Rafin Gora drainage system, Kushaka schist belt, North Western Nigeria

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Abstract: *The Proterozoic Kushaka schist belt of northwestern Nigeria is well known for its alluvial gold occurrence, although the primary source of gold is unknown due to the extensive thick weathering blanket. In this study, we integrate the morphology and microchemistry of alluvial gold to identify the probable primary source of gold in the area. Scanning electron microscope images of gold grains recovered by panning from the Rafin Gora drainage system indicated morphologies that vary from irregular, elongated subrounded, which suggested that they belong to the proximal primary source.The grains shown scorched, pitted, and grooved surfaces that were partly adorned with canals. These features coupled with gold fragments partially detached from the principal grains are indicative of gold grain transportation in a high-energy alluvial system. Polished gold grains show remarkable core-rim zonation with inclusions of galena and pyrite entombed in them. From EMPA analysis the BSe images that the gold grains are dominantly Au-Ag alloys although Cu levels may reach 1.12 wt%. The gold grain fineness values vary between 838 and 998.1 with an average of 933. These compositional characteristics are consistent with primary mineralization linked to orogenic processes. The Ag-rich rims attest to preferential Ag leaching from the margins of the grains, a feature common in alluvial gold grains. Reconnaissance stream sediment compositional data indicate elevated levels of Au-Ba-Ce-Hg-La-Cr-Cu-Mn-Pb-Th-V-Y-Zn a metal associationsuggestive of intrusion-driven hydrothermal quartz vein systems consistent with gold microchemical data. Results obtained in this study provide insight into the nature of gold mineralization and serve as a baseline exploration tool in the Kushaka schist belt in northwestern Nigeria.*

Keywords: *Alluvial gold, morphology, EMPA, microchemistry, stream sediment, geochemistry, Kushaka, Nigeria.*

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1.0 Introduction

Gold particles from alluvial deposits are potent indicator minerals in unveiling their primary sources especially when their morphologies are combined with their compositional diversity (Chapman and Mortensen, 2016; Masson *et al*., 2020; Fominykh *et al*., 2020; Chapman *et al*., 2021; Liu *et al*., 2021; Liu and Beaudoin, 2021). The morphology of an individual gold grain can provide clues to the distance over which they have been transported, while the microchemistry of the grains and the population of mineral inclusions entombed in them reveal their hypogene or primary sources (Chapman and Mortensen, 2006; Chapman *et al*., 2011; McLenaghan and Cabri, 2011). This approach has been employed widely in regions with inadequate rock exposure (Wierchowiec, 2002; Youngson *et al*., 2002; Chapman and Mortensen, 2006; Moles *et al*., 2013; Barrios *et al*., 2015; dos Santos Alves *et al*., 2020). The morphology and surface textures of alluvial gold grains can be utilized to estimate the distance that the gold grains have traveled from their primary source based on the relationship between shape source distances (dos Santos *et al*., 2020). The size and form of placer grains reveal the development and history of their transportation in fluvial environments (Yeend, 1975; Herail *et al*., 1989; Leake *et al*., 1991; Youngson and Craw, 1999; Melchiorre and Henderson, 2019). Therefore, the degree of rounding, polishing, and bending of gold grains can be utilized to determine how far the gold grains have been transported from their primary source (Youngson, 1998; Townley *et al*., 2003; Marquez-Zavalia *et al*., 2004; Masson *et al*., 2021).

The EMPA analytical technique has been used in numerous investigations to connect alluvial deposits to their primary sources (Chapman *et al*., 2021). Gold microchemical signature in the eastern part of Cameroon point to intrusion-related systems and hydrothermal quartz veining as potential sources of hypogene mineralization (Omang *et al*., 2015; Vishiti *et al*., 2015; Ateh *et al*., 2021). Basic, mafic, and ultramafic rocks are the source of placer gold in southern Cameroon (Omang *et al*., 2015, Fuanya et al., 2019; Dongmo *et al.,* 2019). Alluvial gold in northern Cameroon is allegedly derived from granitoid and metasediments of schists that bear numerous quartz veins (Katchaya *et al.*, 2022; Ngoube *et al.*, 2022). In Pakistan, alluvial gold is linked to epithermal mineralization (Alam *et al.*, 2018). Alluvial gold in Portugal is allegedly derived from granitic rocks according to Leal *et al.* (2021). Similar investigations have been used in Russia, to connect economically significant gold placers to their sources (Lalomov *et al.*, 2017; Zaykov *et al.*, 2017; Svetlitskaya *et al.*, 2018; Nevolko *et al.*, 2019). Au-alloy composition has also contributed to paragenetic studies of hypogene mineralization (Parnell *et al.*, 2000; Palacios *et al.*, 2001; Arif and Baker, 2004; Spence-Jones *et al.*, 2018) and in the establishment of the mechanisms by which gold composition is modified in the surficial environment (Hough *et al*., 2009). This approach is used in this study.

Geochemical data from stream sediment has been used in mineral exploration worldwide to pinpoint the vector to mineralized areas (Salminen *et al*., 2008; Omang *et al.,* 2014; Moles and Chapman 2019, Nforba *et al.,* 2020). The practicality of this method pivots on the ease with which multi-element associations found in the sediments may be used to visualize the geology of the catchment (Key *et al.,* 2004; Omang *et al*., 2014). According to Moles and Chapman (2019), two approaches are commonly applied. The first is based on the chemical composition of the fine fraction (usually < 150 µm) and the second relies on the mineralogy and chemistry of the panned concentrate. Panned concentrate may be useful for the immediate identification of ore minerals whose longevity in the surface environment is limited but which may be close to the bedrock source, even though the fine fraction is favoured in regional studies (Moles and Chapman, 2019). An additional understanding of the location and type of gold mineralization can be gained when this is combined with gold-grain investigations. Regional geochemical survey data, once incorporated into the GIS platform, according to Omang *et al*. (2014), do not only express the distribution of the target element but also create a spatial link between numerous elements readily evident. This is particularly helpful when data from the heavy mineral fraction of the stream sediment are also available. The usefulness of stream sediment data in mineral exploration is typically enhanced when gold concentration estimated by the panning and weighing method is combined with stream sediment geochemistry of gold and associated elements (Omang *et al*., 2023; 2014). This is especially true when two-dimensional single-element point symbol maps for displaying elemental spatial distribution and multifractal models are combined with multivariate statistical techniques like factor analysis, cluster analysis, and correlation analysis (Embui *et al.,* 2013; Mimba *et al.,* 2014; Omang *et al.,* 2014; Ghadimi *et al.,* 2016, Nforba *et al.,* 2020).

The Kushaka schist belt is one of the prominent auriferous belts in Nigeria (Oluwakayode *et al*., 2021; Ramadan *et al.,* 2001; Garba, 2002, 2013; Lapworth *et al.,* 2012; Kankara *et al.,* 2016; Abdullahi and Alabi, 2018; Sanusi and Amigun, 2020a, b). In common with many orogenic belts, the abundance and distribution of alluvial gold in this belt provide a powerful indicator of primary gold mineralization although the location of the source remains unclear. The schist belt lies within a complex geologic setting comprising metasedimentary, metavolcanic, and igneous intrusion units which provide the possibility of different styles of primary gold mineralization. It is therefore important to work at determining the possible primary source of gold in the area. This work marks the first time any research to establish the morphology, microtexture, and composition of gold particles in combination with reconnaissance stream sediment geochemistry will be used to trace the possible primary sources of gold mineralization within the Kushaka schist belt. The synthesis of gold composition and stream sediments' geochemical signature will provide a platform for identifying similar deposit types elsewhere.

2.1 Regional geology

The study area forms part of the Kushaka schist belt within the western Nigerian terrane of the Trans-Saharan belt (Fig. 1). The Trans-Saharan belt is a network of Neoproterozoic and older Precambrian rocks formed during the collision between various lithospheric plates, including the West African and Congo Cratons (Omang *et al.,* 2022; Okon *et al.,*2022; Ajibade *et al.,* 1987; Ajibade and Wright, 1989; Dada, 2006). The Trans-Saharan Belt also referred to as the Pan-African Orogenic Belts (Neoproterozoic-Ordovician) is divided into an Eastern Terrane and a Western Nigerian Terrane. The Western Terrane which constitutes the study area is composed of three major lithological units: migmatitic gneisses, supra crustal/schist belts (within the migmatitic gneisses), and plutonic rocks of the Pan-African 'Older Granite Suite' (Fig. 1) (Odigi, 2002; Ajibade *et al.,* 2008; Dada, 2008). The supracrustal/schist belts (including some metavolcanic units) which are best developed in the western part of Nigeria show a general N-S trend. These belts are regarded as upper Proterozoic supracrustal rocks which have been infolded into the migmatite-gneiss-quartzite complex. Some may contain pieces of ocean bottom debris from small back-arc basins (Omang *et al.*, 2022; Woakes *et al.*, 1987). The crystalline basement is overlaid by extensive sedimentary sequences of Mesozoic to Recent age (Ajibade *et al.*, 2008). The sedimentary fill comprises post-orogenic molasse facies and a few thin marine sediments (Adeleye, 1974).

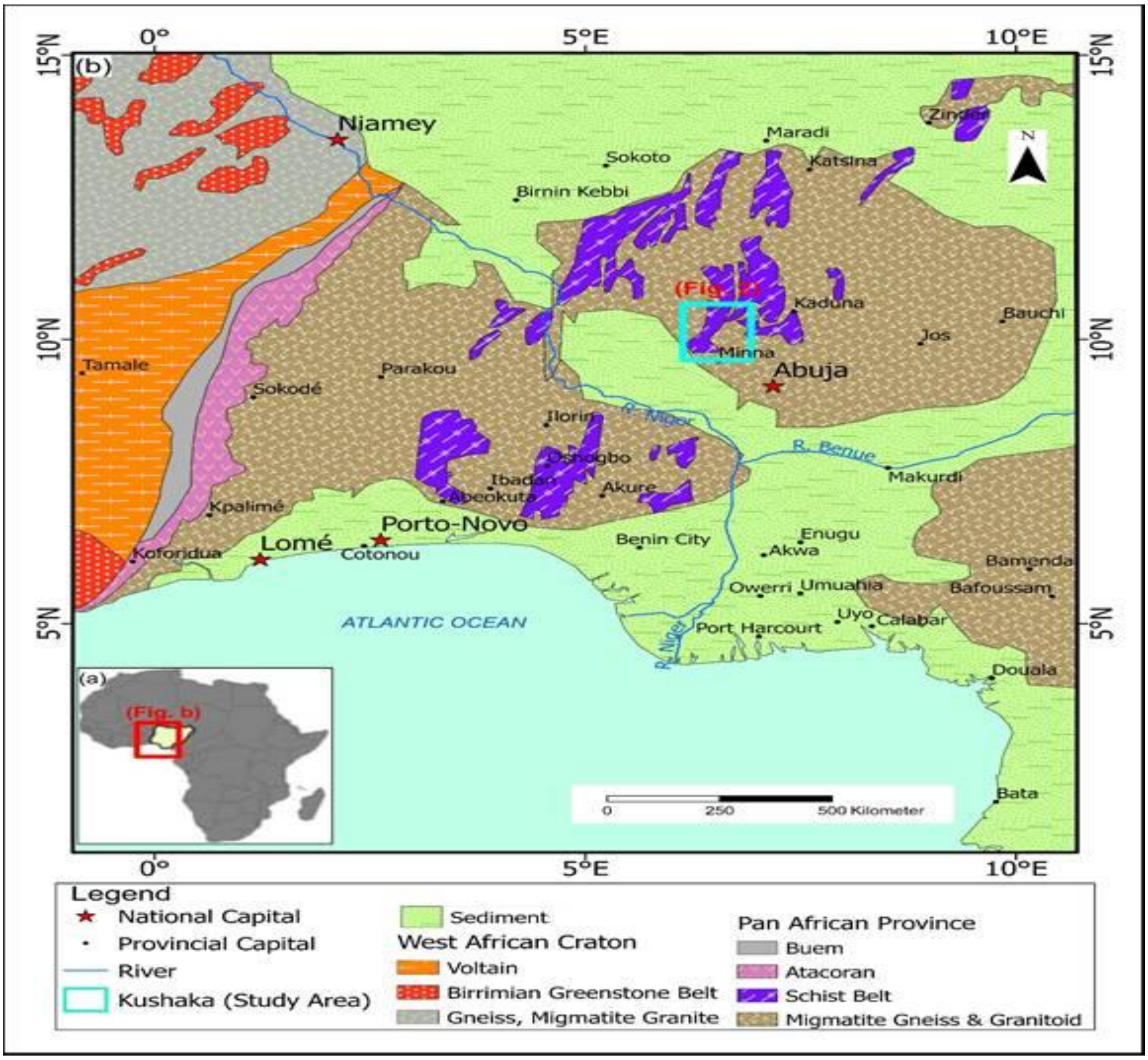


Fig. 1. Simplified geologic map of the Nigerian schist belt on the eastern margin of the West African craton (modified after Turner 1983)

2.1 Local geology

The Late Proterozoic Kushaka schist belt (Fig. 2) is composed predominantly of low-grade metasedimentary and metavolcanic rocks intruded by granitic plutons (Adekoya, 1991; Garba, 2003; Dada, 2008; Oke *et al.*, 2014). According to Ajibade (1980), the schist belt ranges from Kibaran to Pan African (1100-600 Ma). The schist belt is intruded by syn-to late-tectonic granites of

Pan-African ages (Fitches *et al.*, 1985; Ajibade *et al.,* 1989). Lithologically the belt is composed of undifferentiated schist, mylonite, quartzite, sandstone, siltstone, phyllite, gneisses, granite, amphibolites, and pegmatites (Fig. 2). The Kushaka schist belt constitutes part of the Nigerian metallogenic province (Woakes *et al.*, 1987; Obaje, 2009; Garba, 2000; Kankara and Darma, 2016). Within this belt, primary gold occurs in quartz-sulfide (pyrite, chalcopyrite, galena, covellite, and chalcocite) veins and stockworks hosted by amphibolites and gneisses (Garba, 2003). Gold mineralization in this belt is said to be linked to the late Pan-African (500 Ma) orogenic event (Garba, 2000; Wuyep *et al.*, 2007) which postdates regional metamorphism, granitoid intrusion and fracturing (Sanusi and Amigun, 2020a,b). The schist belt is characterized by NE-SW and NW-SE conjugate faults formed due to brittle-ductile deformation during the Late Pan African orogeny (Obaje, 2009; Garba, 2000). These structures serve as pathways for the circulation of hydrothermal fluid.

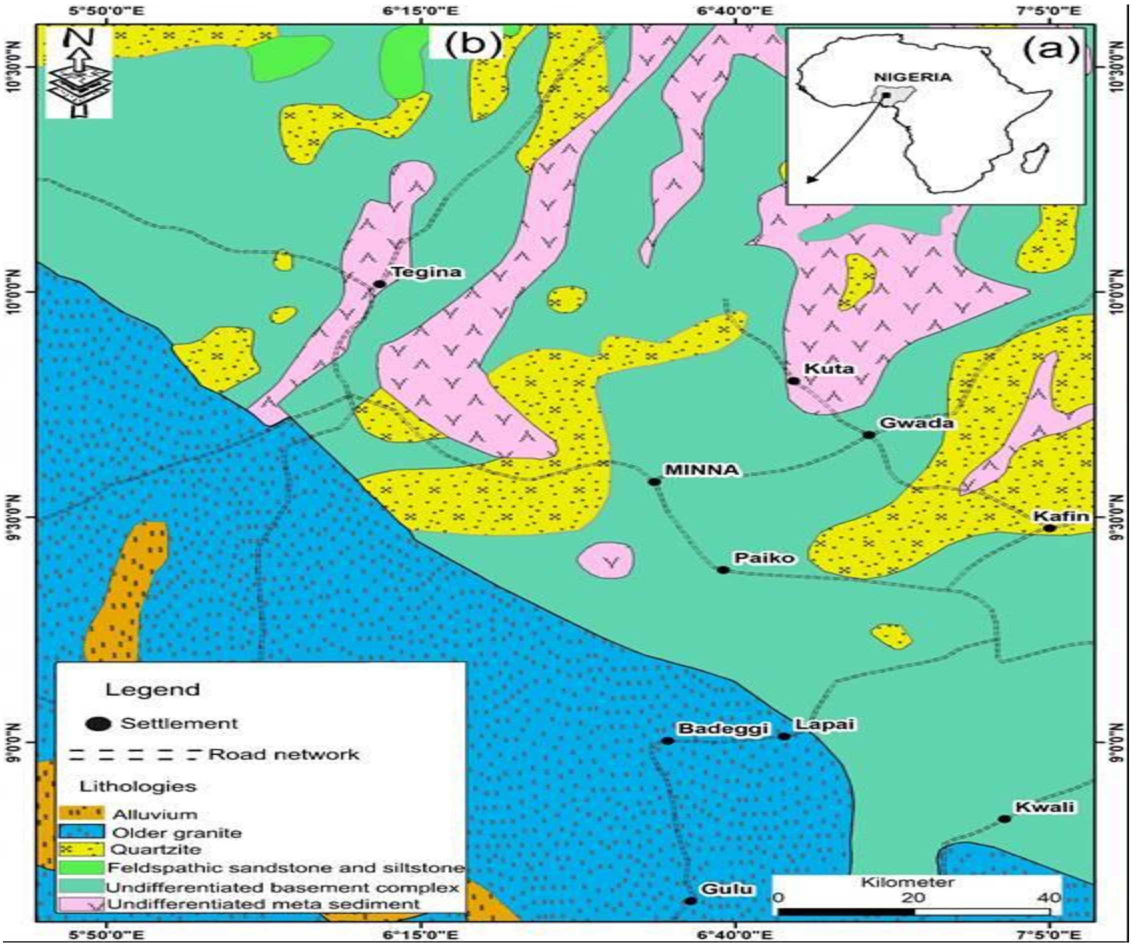


Fig. 2. Geologic map of the Kushaka schist belt north western Nigeria showing the main litholgic units

2 0 Materials and Methods

The stream sediment samples used in this study were collected above stream confluences (Figs. 3 and 4) from five locations within the Rafin Gora drainage system. Samples from first-order streams were favoured because they yield more valuable information on the provenance of placer gold grains from disparate sources. At each sampling site, ~5 kg of active stream sediment samples were collected and panned, and the heavy mineral fraction was retained and stored in a clearly labelled self-sealing plastic bag. A second sample of approximately the same weight was collected and sieved on site and the ≤150 µm fraction was retained. All the sampling sites were located using a GPS and eventually introduced into a GIS. The heavy mineral fraction was dried in the Geology Laboratory, University of Calabar, and the gold grains were handpicked under a binocular microscope. Detrital gold was recovered only from locations 4 and 5.

The gold grains recovered by handpicking

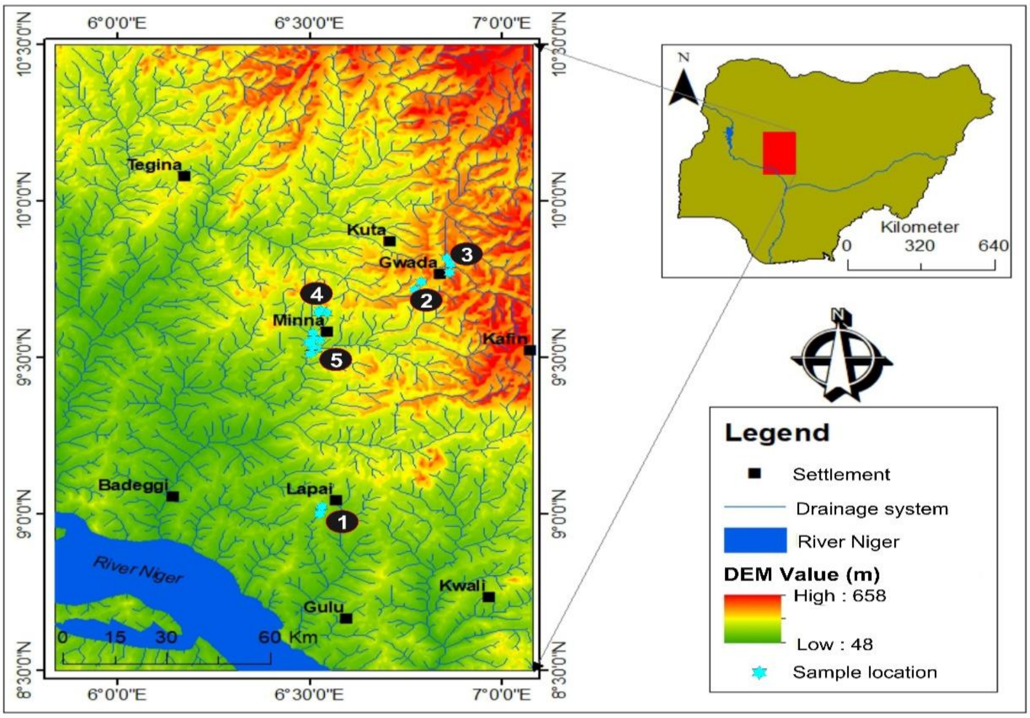


Fig. 3. Drainage map of the Kushaka schist belt Northwestern Nigeria indicating the sample location sites (1-5). Notice the dendritic drainage pattern

were analyzed for their morphology and surface features using the CARLZEISS SUPRA 55 Scanning Electron Microscope (SEM) with an acceleration voltage that varies from 15 to 35 kV in the China University of Geosciences. Care was taken to ensure that artefacts were not introduced during the process of sample preparation. The gold grains selected were mounted in resin blocks and polished with diamond paste. The gold grains were polished using standard procedures. The polished gold grains were examined under an ore microscope as well as the SEM and the mineral inclusions in them were identified and subsequently analyzed for their microchemistry using the JOEL JXA 8230 electron microprobe analyzer (EMPA) equipped with a wavelength dispersive spectrometer WDS at the China University of Geosciences. Instrumental conditions were set at 15 kV, 20 nA beam current, with a 5µm beam diameter and 10-s count time for each element. Background counts were determined by a 10s count-off peak. The grains were analyzed for Au, Ag, and Cu. Standards employed included pure Au, Ag, and Cu. The gold fineness was calculated using the formula Au*1000/Ag + Au (Hallbauer and Utter, 1977).

The ≤150 µm fraction of the stream sediment samples recovered for geochemical analysis was dried, pulverized, and shipped to the ACME Analytical Laboratories, Vancouver, Canada. A 0.5 g of powder quartered from the samples collected where analyzed for Au+53 elements using the inductively coupled plasma mass spectrometry (ICP-MS) technique. The analytical technique permits a detection limit of 0.2 ppb for Au. Randomly selected samples were analyzed twice for quality control while in-house blanks were used to correct for any aliquot impurity. The DSII and OREAS International Standards were used in calibrating the equipment. To evaluate the element association, the inter-element relationship was calculated using the Pearson correlation coefficient.

Fig. 4. Artisanal mining in the study area with the use of rudimentary tools. (a) Artisanal miners panning for gold. (b) Shaking table used for the recovery of gold

3.0 Results and Discussion

3.1 Gold grain morphology and surface textures

The gold particles recovered from the study area show a wide range of shapes and sizes (Figs. 5, 6). Representative gold grains vary in shape from an irregular, elongated, funnel to subrounded (Figs. 5, 6) and in size from 0.5 to 5 mm. The gold grains are zoned (Figs. 5a-g, Figs. 6a, d-f) with characteristic continuous and well-developed rims. The cores are darker compared to the rim and the boundary between the core and the rim is sharp albeit irregular when viewed under the BSE imaging. Ag-depleted zones along solution fissures within some of the grains are present (Figs. 5f, g, l, n, 6). Sulphide inclusions mainly galena and pyrite are entombed in the gold grains (Fig. 6). The gold grains are characterized by fragments partially detaching from the principal grain (Fig. 5 b, c, d, f, j, l, m, n, o). The surfaces of the grains bear cavities, canals, grooves, etched pits, and scratches (Fig. 7). Cavities in the grains are filled with clay.

3.2 Gold grain microchemistry

The composition of the gold grains as determined by EMPA is provided in Figs. 8 and 9. The gold grains are alloyed mainly with Ag although a few analyses have identified Cu. The concentration of gold in the core range from 77.4 to 89.71 wt%, the Ag contents range from 8.1 to 16.20 wt% and the Cu content varies between 0.02 and 1.12 wt% (Fig. 10). Core finenesses range from 838-917.09 (11a). Along the rims, the concentration of gold varies between 98.4 and 101.4 wt%, Ag contents range from 0.12 to 1.60 wt%. The Cu content reaches a maximum of 0.02. wt% (Fig. 10). Rim finenesses vary between 981.14 and 998.81 (11a). The gold grains show an average fineness of 933 (Fig. 11b). The variation in silver content for each sample is presented as cumulative percent in Fig. 12. From the graph,the gold grains reveal four distinct populations represented as (i), (ii), (iii) (iv) while gold grains 1,3-7,9-11 show a similar trend (i), gold grains 2, 8, and 12 show distinct trends represented as (ii), (iii), and (iv), respectively. On the Au-Ag-Cu plot, the gold grains show hydrothermal-orogenic signatures (Fig. 13).

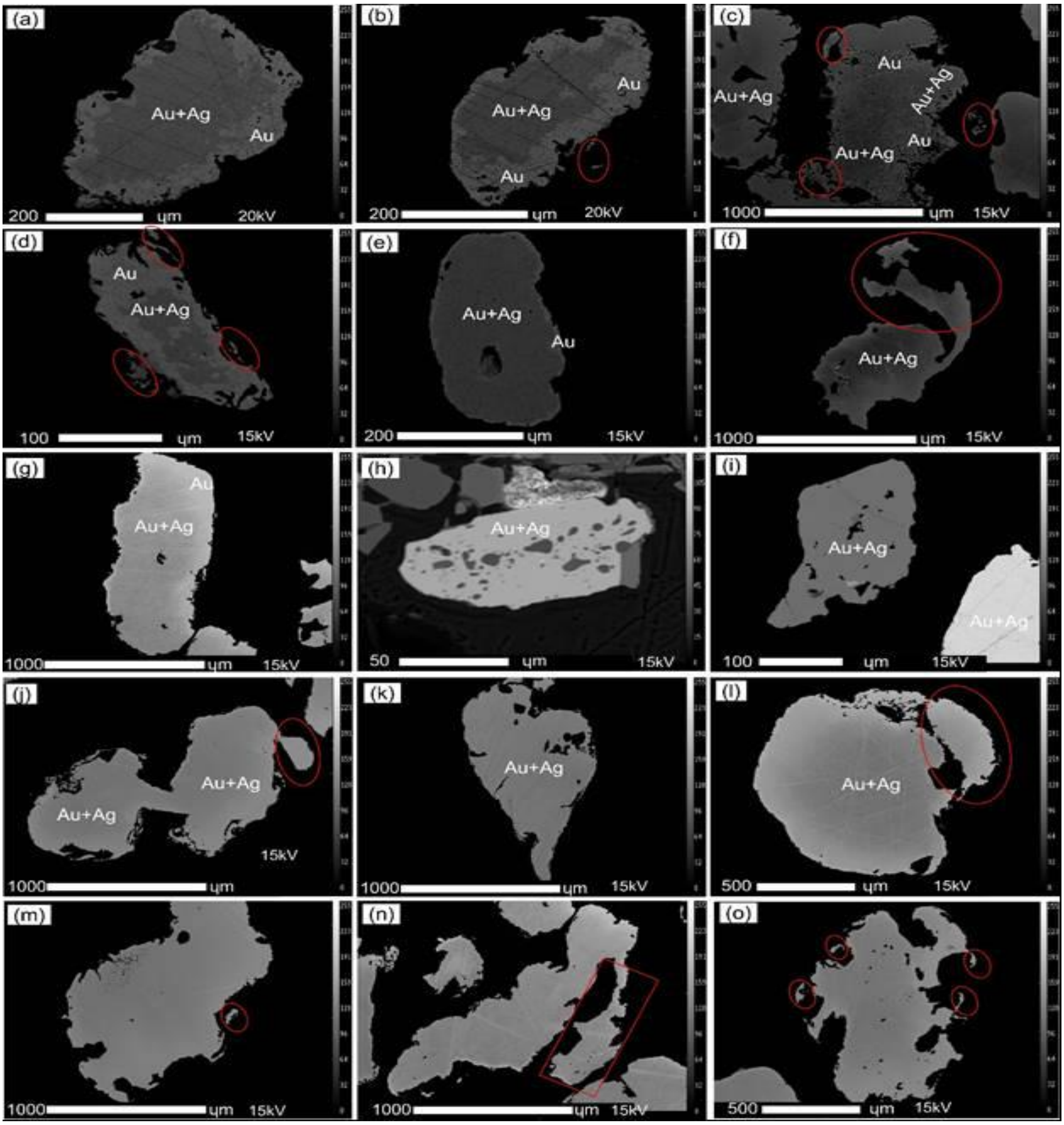


Fig. 5. BSE images of representative gold grains recovered from placer within the Kushaka Schist belt showing a variation in the morphology. The gold grains vary from irregular, elongated, funnel shape to sub-rounded. Take note of fragments partially detached from the principal gold grains.

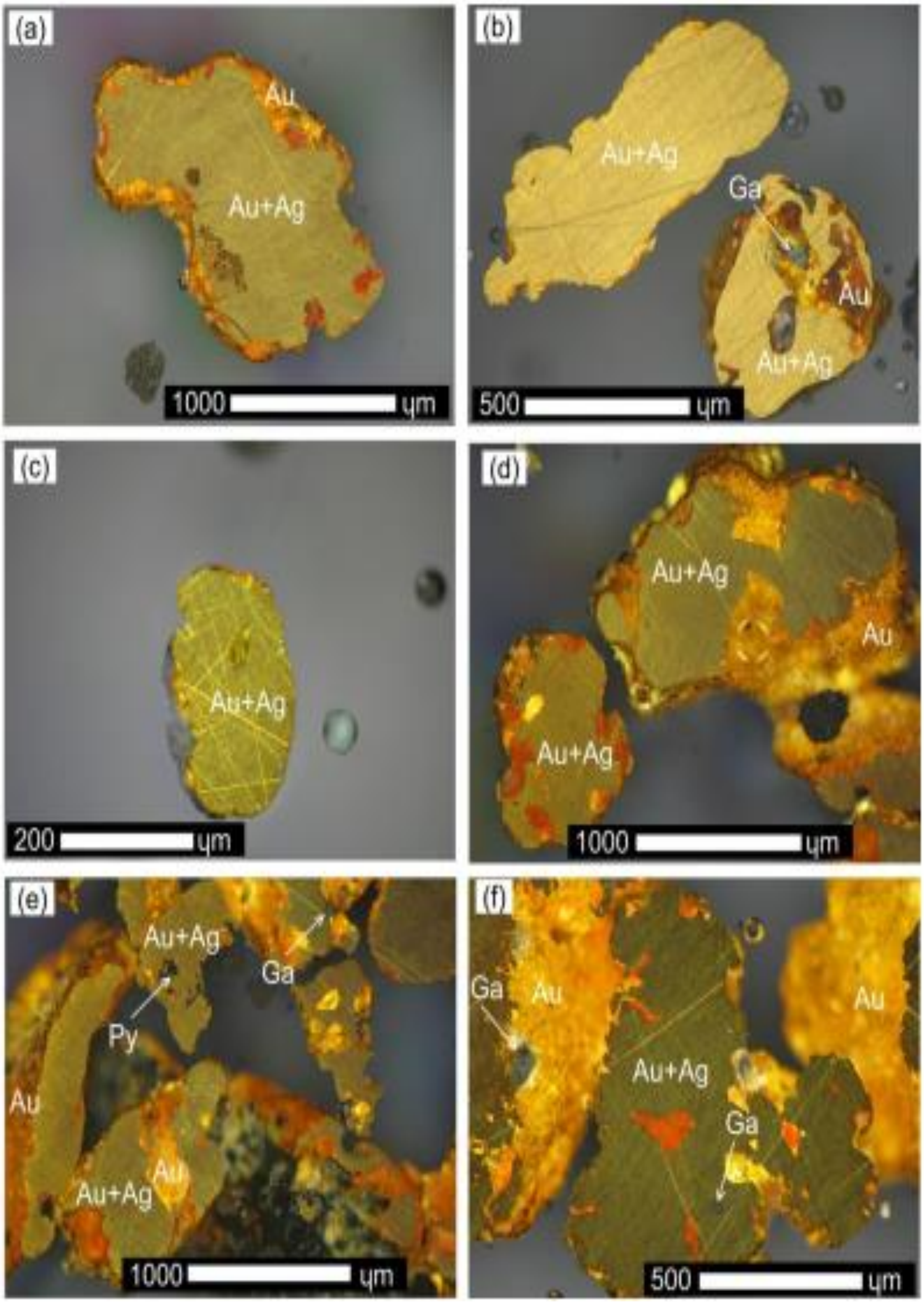


Fig. 6. Photomicrographs in reflected light of representative gold particles from the study area. (a-c) Irregular to sub-round zoned gold grain with a gold-rich rim and a gold - silver rich core. (e-f) Irregular and zoned gold grains. Note solution fissures in the gold gains and pits in the leached zone. Galena and pyrite inclusions are common

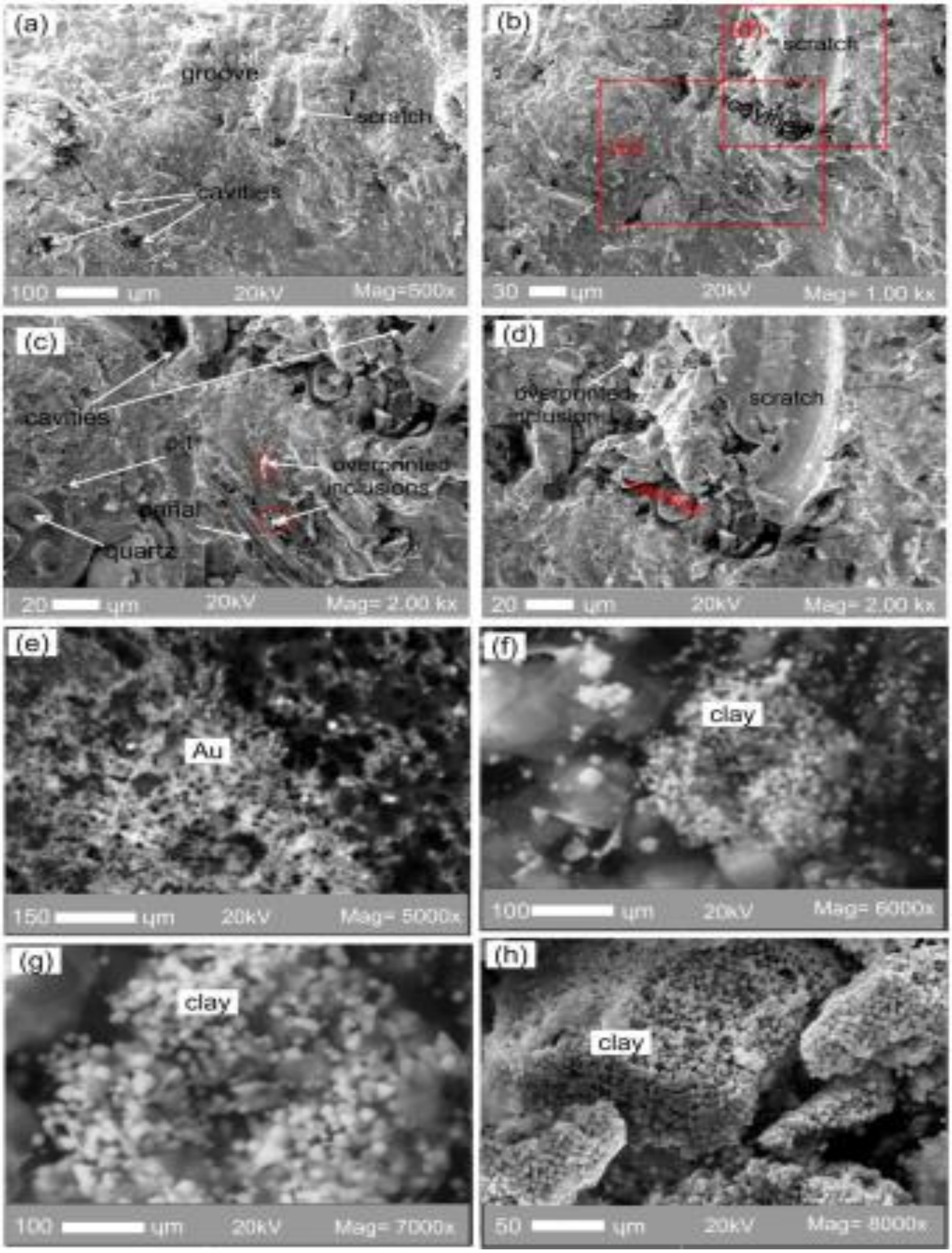
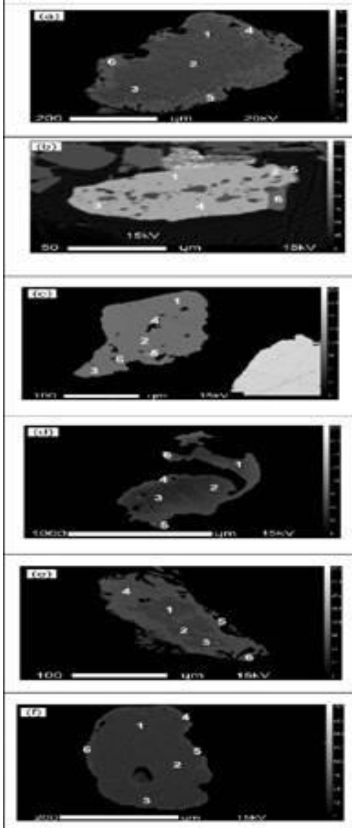


Fig. 7. Characteristic microtexture of the gold grains resulting from physical damage due to impact during fluvial transport



Gold grains	Grain N°	Shape	Point	Position	Content, wt. %				
					Au	Ag	Cu	Total	Fineness
(a)	1	irregular	1	core	88.40	10.06	0.04	98.5	897.6
			2	core	86.35	12.86	0.07	99.28	870.58
			3	core	82.60	11.08	0.02	93.7	881.73
			4	rim	99.27	0.42	0.00	99.69	995.79
			5	rim	100.40	0.82	0.00	101.22	991.90
			6	rim	100.60	0.60	0.00	101.2	994.07
(b)	2	irregular	1	core	81.20	15.60	1.02	97.82	838.84
			2	core	83.40	12.60	0.60	96.6	868.75
			3	core	80.04	10.20	0.80	91.04	886.97
			4	core	82.60	9.42	1.10	93.12	897.63
			5	rim	100.30	1.20	0.01	101.51	988.16
			6	rim	99.72	0.52	0.00	100.24	994.81
(c)	3	irregular	1	core	89.02	16.20	1.12	106.34	846.04
			2	core	88.01	11.12	1.08	100.21	887.82
			3	core	87.03	13.36	0.58	100.97	866.92
			4	core	99.70	1.02	0.00	100.72	989.87
			5	core	100.01	1.12	0.02	101.15	988.93
			6	core	98.40	0.56	0.01	98.97	994.34
(d)	4	irregular	1	core	86.41	10.05	0.68	97.14	895.81
			2	core	87.52	12.52	0.79	100.83	874.65
			3	core	85.50	13.41	0.99	99.9	864.42
			4	rim	99.27	1.60	0.00	100.87	984.14
			5	rim	100.03	0.62	0.00	100.65	993.84
			6	rim	100.40	0.75	0.00	101.15	992.59
(e)	5	elongated	1	core	88.31	9.02	0.55	97.88	907.33
			2	core	86.83	13.42	0.70	100.95	866.13
			3	core	87.61	12.11	0.89	100.61	879.60
			4	core	99.43	1.58	0.00	101.01	984.36
			5	rim	100.01	1.27	0.00	101.28	987.46
			6	rim	101.40	0.80	0.00	102.2	992.17
(f)	6	euhedral	1	core	80.44	14.20	1.04	95.68	849.90
			2	core	82.64	11.60	0.80	95.04	876.01
			3	core	81.04	11.20	0.03	92.27	878.68
			4	rim	99.24	0.30	0.00	99.54	996.66
			5	rim	100.02	0.53	0.01	100.55	994.73
			6	rim	100.40	0.20	0.00	100.6	998.01

Fig. 8. BSE images of alluvial gold grains recovered from location 4 in the Rafin Gora drainage together with their corresponding micro chemical signature. Notice the gold rich rims and Ag poor cores

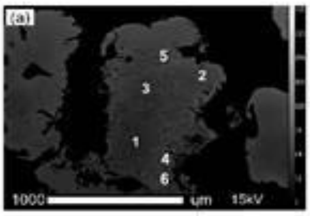
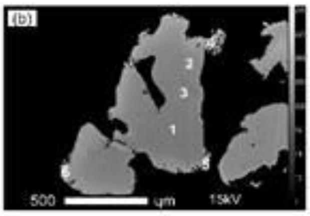
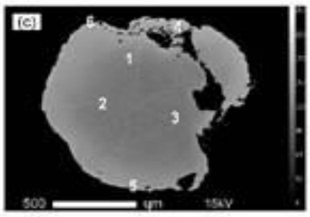
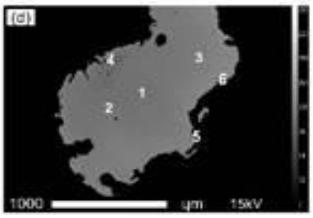
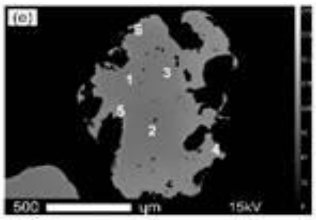
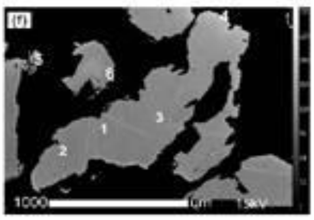
Gold grains	Grain N°	Shape	Point	Position	Content, wt. %				
					Au	Ag	Cu	Total	Fineness
	7	irregular	1	core	82.13	10.16	0.07	92.36	889.91
			2	core	86.21	11.32	0.02	97.55	883.93
			3	core	85.28	10.21	0.07	95.56	893.03
			4	rim	100.27	0.51	0.00	100.78	994.94
			5	rim	101.22	0.74	0.00	101.96	992.74
			6	rim	100.80	0.50	0.00	101.3	995.06
	8	irregular	1	core	79.59	11.64	0.88	92.11	872.14
			2	core	77.40	10.32	0.60	88.32	882.35
			3	core	82.14	11.31	0.73	94.81	878.97
			4	rim	81.41	10.12	0.98	92.51	889.44
			5	rim	100.56	0.97	0.02	101.55	990.45
			6	rim	99.92	0.77	0.01	100.7	992.35
	9	subrounded	1	core	87.13	12.20	1.01	100.34	877.18
			2	core	87.01	10.23	1.00	98.24	894.80
			3	core	85.01	11.43	0.44	96.88	881.48
			4	rim	100.70	1.15	0.00	101.85	988.71
			5	rim	101.02	0.52	0.01	101.55	994.88
			6	rim	99.50	1.56	0.00	101.06	984.56
	10	irregular	1	core	83.22	12.05	0.87	96.14	873.52
			2	core	89.71	10.12	0.81	100.64	898.63
			3	core	89.71	11.21	0.88	101.81	888.92
			4	rim	99.44	0.61	0.01	100.06	993.90
			5	rim	101.01	0.71	0.00	101.72	993.03
			6	rim	100.01	0.65	0.01	100.67	993.54
	11	irregular	1	core	89.11	10.11	0.56	99.78	898.11
			2	core	87.01	12.12	0.60	99.73	877.74
			3	core	85.55	10.12	0.72	96.39	894.22
			4	rim	100.43	1.02	0.00	101.45	989.95
			5	rim	101.02	1.07	0.00	102.09	989.52
			6	rim	100.40	0.50	0.00	100.9	995.04
	12	irregular	1	core	85.20	9.11	0.44	94.75	903.40
			2	core	87.22	14.21	0.60	102.03	859.90
			3	core	89.60	8.10	0.88	98.58	917.09
			4	rim	100.80	0.12	0.01	100.93	998.81
			5	rim	101.30	0.33	0.02	101.65	996.75
			6	rim	100.02	0.60	0.00	100.62	994.04

Fig. 9. BSE images of alluvial gold grains recovered from location 5 in the Rafin Gora drainage together with their corresponding micro chemical signature. Take note of gold rich rims and Ag poor cores

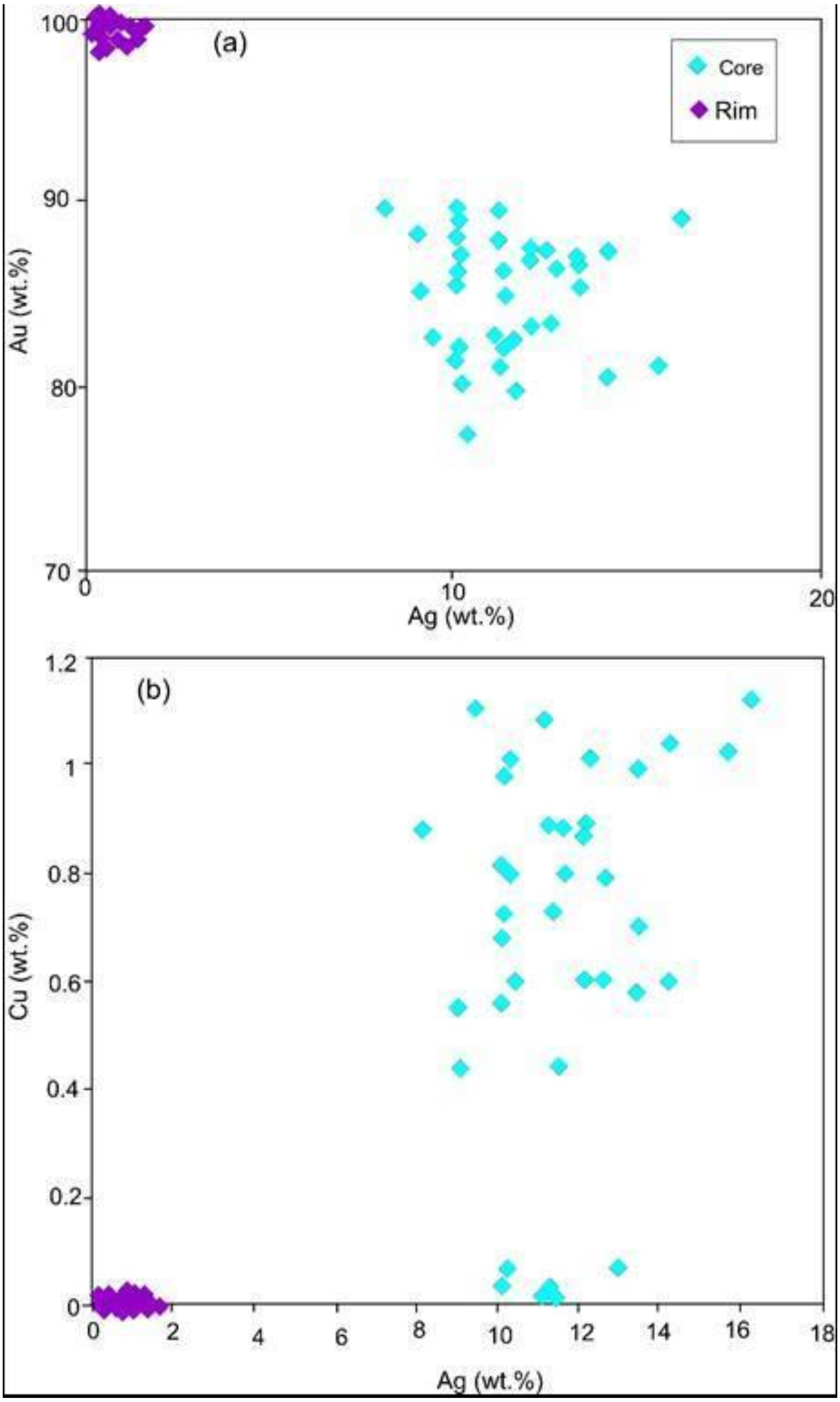


Fig. 10. (a) Co-variance of Ag and Au for gold particles from the Rafin Gora drainage, Kushaka schist belt northwestern Nigeria. (b) Co-variance of Ag and Cu for gold particles from the Rafin Gora drainage, Kushaka schist belt north western Nigeria

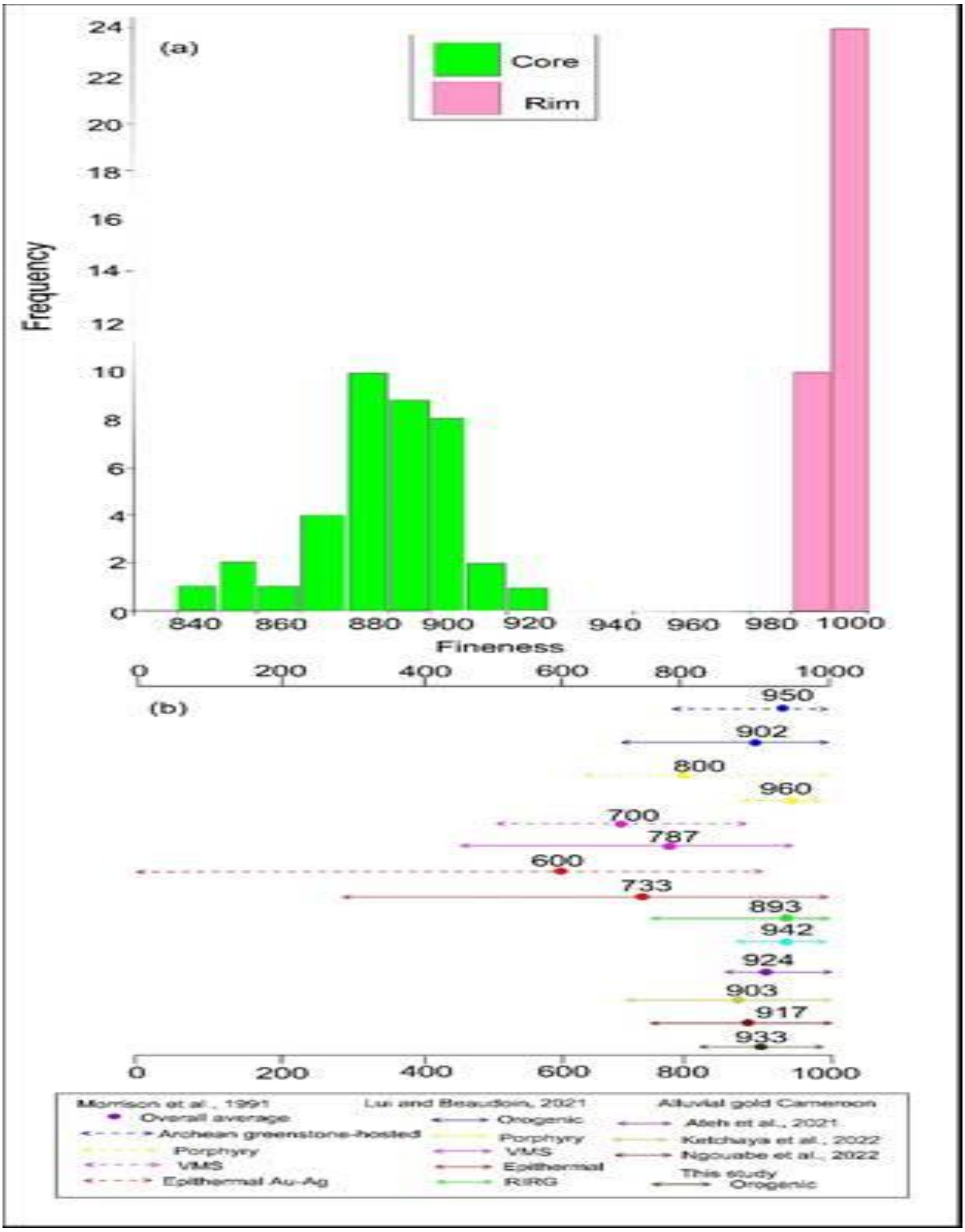


Fig. 11. (a) Histogram of fineness for Au grains from the Rafin Gora drainage, Kushaka schist belt north western Nigeria. (b) Comparison of range and overall average of gold fineness from this study and literature data. The fineness data for Archean greenstone-hosted, porphyry, VMS, and epithermal Au-Ag deposits is from (Liu & Beaudoin, 2021, Morrison *et al*. 1991).

4.3 Stream sediment geochemistry

The geochemical composition for the suite of elements analyzed alongside gold in the stream sediment is given in Table 1. Besides Fe which showed a maximum concentration of 6.6 wt%, the concentrations of major oxides are generally very low. Gold contents attain a maximum of 21.18 ppm although sporadic occurrences exceeding 1 ppm have been identified. This is coupled with elevated contents in elements such as Ba-Ce-Cr-Cu-La-Mn-Pb-Th-V-Y-Zn. The chalcophilic elements (Cu, Pb, and Zn) have concentrations that span from 1.82 to 176.3 ppm. The sediments showed a concentration of Pt that up to 0.002 ppm. The inter-element relationship calculated using the Pearson correlation coefficient is given in Table 2. It is clear from the correlation matrix that the pathfinder elements for gold in this study include Mn, Sr, V, and Zr (Table 2).

Table 2: Correlation…………………..

Sample ID	LD.Limit	L1S3	L1S4	L2S2	L2S3	L2S6	L3S1	L3S3	L3S6	L4S1	L4S2	L4S4	L5S1	L5S2	L5S3	L5S8	L5S9	L5S10	L5S11
Major element wt%																			
Al_2O_3	0.01	0.54	0.63	0.81	0.34	0.72	0.7	0.19	0.22	0.41	1.21	0.15	0.13	1.26	0.13	0.23	1.19	0.07	0.3
Fe_2O_3	0.01	3.08	4.03	3.5	1.87	4.68	3.46	2.71	2.85	6.6	2.83	1.87	1.98	3.19	2.17	2.55	3.4	1.9	4.04
MgO	0.01	0.01	<0.01	0.01	0.13	<0.01	0.32	<0.01	0.01	0.03	0.41	0.01	0.01	0.47	0.01	0.02	0.47	<0.01	0.03
CaO	0.01	0.06	0.03	0.03	0.04	0.03	0.34	0.04	0.05	0.25	0.3	0.06	0.06	0.21	0.07	0.09	0.54	0.03	0.22
Na_2O	0.001	0.002	0.003	0.001	0.004	<0.001	0.005	<0.001	0.002	0.002	0.009	0.002	<0.001	0.008	0.002	0.002	0.013	<0.001	0.002
K_2O	0.01	0.02	0.02	0.02	0.1	0.02	0.33	<0.01	0.01	0.01	0.45	0.01	<0.01	0.5	<0.01	0.01	0.51	<0.01	0.01
TiO_2	0.001	0.11	0.056	0.052	0.255	0.044	0.099	0.144	0.261	0.615	0.143	0.387	0.42	0.13	0.314	0.3	0.163	0.336	0.528
P_2O_5	0.001	0.016	0.012	0.007	0.009	0.013	0.026	0.064	0.137	0.015	0.019	0.198	0.123	0.018	0.14	0.148	0.028	0.156	0.008
SO_3	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.05	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.04	<0.02	<0.02
Trace element ppm																			
Au	0.0002	0.025	0.002	0.0099	3.2684	0.0077	0.0083	0.0409	2.1078	21.1844	0.2133	0.255	1.4081	0.0098	0.0584	0.0315	0.0094	0.0058	1.7885
Ag	0.0002	0.032	0.007	0.019	0.519	0.014	0.045	9	0.217	5.334	0.053	0.018	0.039	0.044	0.006	0.014	0.066	<0.002	0.182
As	0.1	0.8	7.1	1.7	1.1	6.2	1.9	1.2	1.7	0.3	1.3	1.4	0.7	1.7	1	1.5	1.6	1.8	0.3
B	20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Ba	0.5	90.7	15.6	61.2	92.4	19.4	85.9	11.3	11.9	22.2	153.7	47.2	29.7	157.9	24	14.2	117.6	13.2	19.1
Be	0.1	0.5	0.6	0.6	0.2	0.8	0.3	0.3	0.3	0.1	0.5	0.3	0.2	0.6	0.2	0.3	0.4	<0.1	<0.1
Bi	0.02	0.08	0.09	0.09	0.06	0.08	0.07	0.11	0.13	5.29	0.13	0.13	0.12	0.1	0.11	0.26	0.09	0.12	2.59
Ce	0.1	259.7	91.4	93.6	64.8	47.8	25.3	1213.3	>2000.0	443.1	56.5	>2000.0	>2000.0	49	>2000.0	>2000.0	56.6	>2000.0	155.5
Co	0.1	17.2	10.6	17.3	19.4	19	23.4	5.1	5.3	5.9	15.5	5.7	3.1	15.9	2.7	3.3	19.1	2.4	5.5
Cs	0.02	0.29	0.25	0.51	0.36	0.32	0.47	0.08	0.09	0.09	0.67	0.08	0.02	0.77	0.03	0.1	0.66	0.05	0.07
Cr	0.5	108.9	236.7	80.1	22.2	234.1	45.9	48.4	48.9	36	72.3	29.3	33.5	75.8	29.5	34.8	56.6	28.5	34.6
Cu	0.01	17.3	28.44	19.67	36.53	27.4	74.34	17.79	12.57	7.52	36.86	12.08	4.69	38.33	5.54	7.52	54.41	1.82	17.3
Cd	0.01	<0.01	<0.01	<0.01	0.05	<0.01	0.05	<0.01	<0.01	0.07	0.03	<0.01	<0.01	0.03	<0.01	0.01	0.08	<0.01	0.05
Ga	0.1	3.5	5	5.4	2.1	6.2	3	1.5	1	3.8	5	<0.1	<0.1	5.3	<0.1	1.1	4.2	0.8	2.5
Ge	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Hf	0.02	0.15	0.17	0.19	0.18	0.19	0.11	0.08	0.08	0.32	0.15	0.08	0.1	0.15	0.06	0.08	0.16	0.1	0.21
Hg	0.005	0.246	0.111	0.262	0.044	0.182	0.248	2.86	0.558	3.436	0.085	0.171	0.261	0.1	0.031	0.086	0.424	0.04	76

5 Discussion

5.1 Gold gain morphology and proximity to primary source

The mechanism of transportation, nature, location of primary gold mineralization sources as well as modification inherited by the gold grains during the process of transportation have been studied worldwide using gold grain morphology, surface texture, mineral inclusions, Ag content, and crystal imprints inherited in the surficial environment (Knight *et al.,* 1999a,b; Mikulski and Wierchowiec, 2013; Moles *et al.,* 2013; Barrios *et al.,* 2015; Lalomov *et al.,* 2017; Alam *et al.,* 2018; Wierchowiec *et al.,* 2021; Ketchaya *et al.,* 2022). These criteria have been used in the Kushaka schist belt, Northwestern Nigeria to evaluate the distance-to-source of gold grains recovered from the Rafin Gora drainage system.The SEM images indicated that the grains vary in shape from irregular, elongated, and funnel-like to sub-rounded (Figs. 5 and 6). Gold grains are liberated directly from the primary source are generally irregular in shape (Omang *et al.,* 2015; Katchaya et al., 2022; Ngouabe *et al.,* 2022). The irregular shape of the gold grains indicates their deviation from a source relatively close to the sampling point since the grains are inferred to have experienced little attrition and deformation (Figs. 5 and 6). The gold grains were then modified by physical and chemical weathering during the process of transportation (Knight *et al.,* 1999a, b), thereby revealing distinct morphological changes. Their elongated, funnel-like, and sub-rounded nature was inherited as the gold grains were transported downstream (Melchiorre *et al.,* 2017; Melchiorre and Henderson, 2019). Sub-rounded grains encountered in the samples are an indication of longer transport distance.

During the transportation of the gold grains and depending on the type of sediment energy and composition of fluvial transport, the physical and chemical modification imprints marks indicating the effect of supergene impacts, whereas the hypogene mineralogy is represented by central alloy compositions and inclusions of sulphides and other minerals (Chapman *et al.,* 2010; 2011). Most of the gold grains are characterized by tearing and fragments detaching from the principal gold grains (Fig. 5). These provide evidence for grain size reduction, physical hammering, abrasion of large pebbles, and chemical modification during transportation (Knight *et al.,* 1999a,b; Ngouabe *et al.,* 2022) in high energy streams (Yeend, 1975). According to Ateh *et al.* (2021), the progressive transformation of the grains over time in streams detaches the inclusions, rounds edges, smooths, and infolds protrusions, and increases the fatness of the grains. Such dynamic conditions may explain the occurrence of cavities in the grains (Chapman *et al.,* 2002). Cavities partially or entirely left evoke mechanical dislodgement or disaggregation of gangue minerals such as quartz, apatite, and monazite due to their hardness and resistance to abrasion during transport; but also, the action of dissolution considering chemical instability of minerals, such as calcite and pyrite (Ngouabe *et al.,* 2022). These voids could also act as detachment zones as shown in (Fig. 5), thus leading to the breakdown of the gold grain mass. Small inclusions of sulphide minerals represent the associated hypogene mineralogy (Fig. 5).

The gold grains exhibit Au-rich zones developed along the rims and solution fissures. The cores of the gold grains are more enriched in Ag (Figs. 5, 6). These features have been reported in alluvial and eluvial systems (Mann, 1984; Colin and Vieillard, 1991; Suh and Lehmann, 2003; Nakagawa *et al.,* 2005; Omang *et al.,* 2015) and are interpreted to represent preferential and selective Ag dissolution and leaching during fluvial transportation and mechanical reworking of grains. The selective leaching of Ag also contributes to the high fineness of the rim, while the core has a high concentration of Ag + Au which represents the composition of the primary gold (Figs. 7, 8). Silver has a higher solubility than gold, particularly in acid chloride solution (Mann, 1984; Colin and Vieillard, 1991). The gold grains show no evidence of secondary growth. The core-rim boundary is serrated and gradational and there is no pure Au overgrowth. The gold gains seem to have been transferred directly from the primary source into the fluvial networks and the composition of the cores, therefore, represents the hypogene composition (Loen, 1995; Lange and Gignoux, 1999; Chapman et al., 2000a). Since rim development is regarded as a secondary phenomenon only the composition of the core has been used in deducing the mineral system.

5.2 Gold grain microchemistry

The compositions of gold grains have been used as a guide to indicate a source deposit type (Chapman *et al.*, 2021). The investigation of Au-alloy composition has contributed significantly to studies of primary mineralization (Palacios et al., 2001; Chapman et al., 2021). This provides details on the processes occurring in the surface environment and contributed to modifying the gold composition (Hough *et al.,* 2009). However, Ag is ubiquitous as an alloy component Cu is recorded only sporadically in grains from the Kushaka schist belt with concentrations that reach a high of 0.02 wt% in the rims. The alloyed gold within the alluvial gold grains was investigated within the core and rims of each gold particle. The grains show Au contents that approached 101.4 and Ag contents that reach a maximum of 16.20 wt% in the core. This is linked to an average gold fineness of 933 which corresponds to a gold fineness from studied orogenic deposits defined by Morrison *et al*. (1991) and by Liu and Beaudoin (2021). Placer gold related to magmatic events has also been fingerprinted using the Cu content of the gold grains (Moles *et al*., 2013). Cu concentrations as high as 1.12% revealed by the EMPA analyses of the grains suggest at least in part the involvement of magmatic fluids possibly related to the granitic plutons in the ore-forming process. Gold fineness in combination with Cu concentration in placer gold grains has been used in differentiating primary gold in the Klondike District in Yukon Territory Canada (Chapman *et al.,* 2010). To identify populations within the gold particles the cumulative percentile vs increasing Ag plot (Leake *et al.,* 1998; Chapman *et al.,* 2000a, b) was used. The plot reveals four populations of gold grains (Fig. 12) from the same source. According to Townley *et al.* (2003), the gold compositional field used in inferring the mineralization styles and evolution of the mineralizing fluids (Chapman *et al.,* 2000a,b) the gold in the study plots around the hydrothermal-orogenic field (Fig. 13).

Analysis of stream sediments from the Kushaka Schist belt reveals gold with a concentration as high as 2.18 ppm. This is coupled with elevated contents of Ba-Ce-Hg-La-Cr-Cu-Mn-Pb-Th-V-Y-Zn. This association indicates granitic intrusions associated with sulfide-quartz vein-dominated mineralization. Gold and related base metals with granitic provenance have been reported in Pakistan (Mateen *et al.,* 2022). Y/Ni ratios that vary from 0.25 to 58.47 for the stream sediment also support the granitic source for gold in the schist belt (Mateen et al., 2022). The occurrence of Mo in association with chalcophilic elements such as Cu-Zn (r = 0.86) revealed in the sediment can be related to hydrothermal alteration linked to sulphide mineralization in the study area (Naseem *et al*., 2002). The occurrence of gold in association with Mn as V is thought to be influenced by the hydrothermal protolith that intruded the country rocks through the shear zones (Martins-Ferriera *et al*.,2017) suggesting that the gold may be connected to deep-seated igneous hydrothermal processes (Chapman *et al.,* 2011). The exploration strategy to be used in the area must take into account the various episode of hydrothermal veining that has contributed to the Au emplacement, as this model suggests that the emplacement of granitoid, sulfide deposition, and gold mineralization are not contemporaneous (Embui *et al*. 2013).

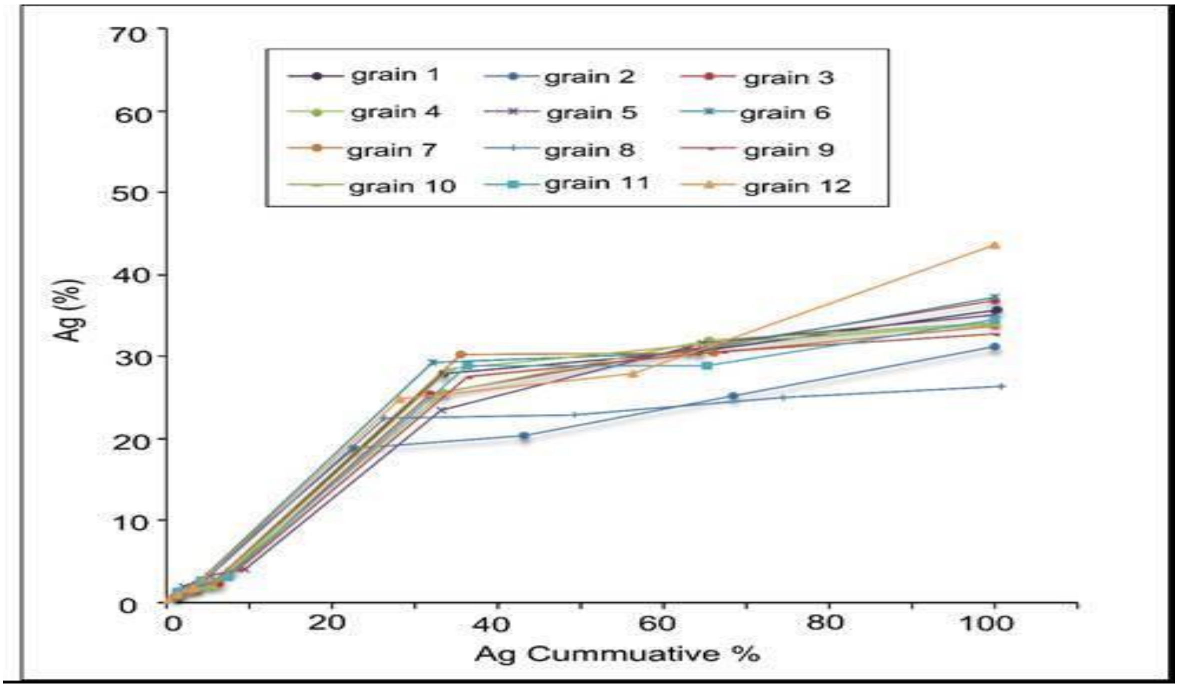


Fig. 12. Ag content variation of alluvial gold grain population from Rafin Gora drainage Kushaka schist belt, north western Nigeria. Notice a single population of gold grains from a homogenous hypogene

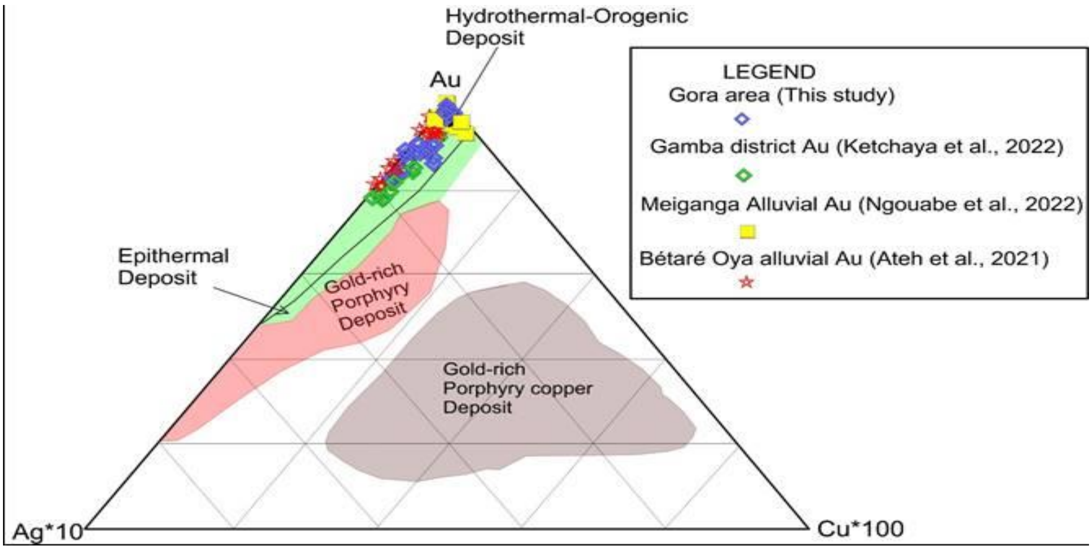


Fig. 13. Ternary Au-Cu-Ag plots of the compositions of Au grain from the Rafin Gora drainage, kushaka schist belt northwestern Nigeria compared with those from the Kazikkaya Turkey lode gold, Hunker dome lode, Grasberg, Indonesia, Santo Tomas II, Philippines, and Cerro Casale gold porphyry northern Chile. Gold grains from the Rafin Gora drainage show hydrothermal, orogenic/or intrusion-related signatures

5.0 Conclusions

The following conclusions can be drawn from this study

1. Gold grains recovered from the Rafin Gora drainage within the Kushaka schist belt are single native gold grains. They vary in morphology from irregular, elongated, funnel shape, to sub-rounded. This indicates their derivation from proximal sources. The micro textures observed indicate transportation in a high-energy environment. The gold grains lack evidence of epigenetic origin in the secondary environment thus the composition of the cores should be similar to those of the primary gold.
2. The gold particles have rims and solution fissures with low silver content despite their proximity to the hypogene source. This we interpret to be due to the selective leaching of silver by weathering fluids, a phenomenon common in alluvial systems.
3. The gold grains are Au-Ag alloys with minor amounts of Cu. The lack of internal compositional variation in core composition suggests the mineral systems involved a single gold precipitation event.
4. The gold grains reveal four populations from a homogenous source with an average fineness of 933. This coupled with Au-Ag-Cu ternary plot reveals a hydrothermal-orogenic source for the gold grains.
5. Stream sediment geochemistry has identified gold in association with elements such as Ba, Ce, Hg, La, Cr, Cu, Mn, Pb, Th, V, Y, Zn. This can be linked to intrusion-related hydrothermal quartz vein-sulfide mineralization. The pathfinder elements in the area include Mn, Sr, V, and Zr.

Acknowledgement

This work is part of an attempt to study the alluvial gold system in northern and western Nigeria. Part of the data used in this study constitutes the M.Sc dissertation of GTK whose data forms part of this contribution. Dr. Isah Aliyu Goro of the Federal University of Technology Minna is acknowledged for his support during the fieldwork. **5.0 References**

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Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

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BOO, GTK, and EAE carried out the field study and sample collection. AV, MEO, and BOO processed the data and initiated and wrote the first draft of the manuscript. CES in cooperation with BOO conceived the study and guided the analytical procedures for all the samples and reviewed, read, and approved the manuscript. All authors contributed in writing, editing, and revising the manuscript under the direction of CES.