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Geochemical prospecting of polymetallic mineralization in Gimbi-Nejo area, West Ethiopia

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ABSTRACT

It is strongly believed that tremendous resources of precious metals and oxides are hidden in the West Ethiopian region. The present work presents a significant test to conduct oriented geochemical mapping for forty-two elements combined with typical geological features in the Pan-African basement exposed area using stream sediment and rock samples. The stream sediments most likely contain some elements directly derived from the surrounding Precambrian to Tertiary bedded metamorphic and igneous intrusive rock units. The obtained data suggest high economic potentials for Au (2.14 ng/g), Cu (43.56 μg/g), Cr (365.1 μg/g), Ni (69.2 μg/g), Co (34.46 μg/g), V (204.1 μg/g), Ti (13278 μg/g), Mn (1472 μg/g), Fe₂O₃ (10.97 %), P (888 μg/g), Al₂O₃ (14.05 %), Ba (501.7 μ g/g), Zr (309.5 μ g/g), Sr (155.7 μ g/g), and Nb (28.2 μ g/g). In the composite geochemical anomalies maps, anomalous zones HS12, HS16, HS18, HS19, HS20, and HS28 suggest that transitional metals of intense differentiation with high average contents as compared to Chinese recommended values may be the favourable focus of exploration in the migmatitic gneiss (Cu \sim 66.38 μg/g), granitic orthogneiss (Zr \sim 426.9 μg/g), upper basalt/lower basalt (Nb ~ 63.4 µg/g), meta-volcanic (Mn ~ 2680 µg/g, Ti ~ 29823 µg/g, V ~ 365.6 µg/g, Fe₂O₃ \sim 1629 %), meta-sedimentary formation (Au \sim 5.3 ng/g), Abshala tectonic melange (Cr \sim 2457.1 µg/g), and meta-ultrabasic rocks (Co ~ 62.65 μg/g, Cu ~ 66.38 μg/g, Ni ~ 313.4 μg/g). In conclusion, fifteen ore-forming elements are distinctively abnormal in the area with sixty-four new discovered mineralized spots.

1. Introduction

Stream sediments, especially their geochemistry, may indicate their source lithology ([Young et al., 2013; Kirkwood et al., 2016](#page-19-0)), thus making them a strategic exploration tool ([Fletcher, 1997](#page-18-0)). Stream sediment-based prospecting is commonly useful in areas with various drainage system ([Nforba et al., 2020](#page-19-0)). Geochemical mapping has been effectively used to describe significant mineralization in the region of high to low relief, and in complicated geological settings ([Chandrajith](#page-18-0) [et al., 2001](#page-18-0)). In many countries, this type of work is commonly utilized based on a variety of medium, such as stream sediments, soils, rocks, etc. ([Darnley, 1990; Reimann et al., 1998; Rice, 1999; Key et al., 2004;](#page-18-0) [Salminen et al., 2005\)](#page-18-0).

Literature reviews show that both basic geology and mineral resources in Ethiopia are relatively not extensively investigated. The

general reviews of Ethiopian industrial minerals were published only before the 21st century by [Hamrla \(1978\)](#page-18-0), [Knot and Abera \(1983\),](#page-19-0) [Sabov et al. \(1983\)](#page-19-0), [Getaneh and Saxena \(1984\)](#page-18-0), [Getaneh \(1985\)](#page-18-0), [Mengistu \(1987\)](#page-19-0), [Mengistu and Fentaw \(1993,](#page-19-0) [1994,](#page-19-0) [2000\)](#page-19-0), [Abera](#page-18-0) [\(1994\),](#page-18-0) [Fentaw and Mengistu \(1998\),](#page-18-0) and [Fentaw and Mohammed](#page-18-0) [\(1999\).](#page-18-0) The Ethiopian crystalline basements contain almost all wellknown mineral commodities of the country ([Tadesse et al., 2003\)](#page-19-0). A new metallogenic province of epithermal-type gold mineralization has been recently discovered in the Ethiopian rift zone ([Tadesse, 2000,](#page-19-0) [2001\)](#page-19-0). Most of gold deposits in north and south Ethiopia have been successively studied by [Billay et al. \(1997\), Deksissa and Koeberl \(2002,](#page-18-0) [2004\),](#page-18-0) and [Tadesse \(2004\)](#page-19-0). Similarly, nickel and cobalt deposits in southern Ethiopia have also investigated by [Goossens \(2000\),](#page-18-0) and [Selassie and Reimold \(2000\)](#page-19-0). Geological terrains can be evaluated by a stream sediment survey [\(Ranasinghe et al., 2009\)](#page-19-0), allowing discovery of

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Fig. 1. The tectonic map of the Arabian-Nubian Shield shows the project area's location, Gimbi-Nejo west Ethiopia (modified after [Stern et al., 2005](#page-19-0); [Woldemichael](#page-19-0) [et al., 2009](#page-19-0); [Johnson et al., 2011; Ghebretensae et al., 2019\)](#page-18-0).

ore deposits. The western Ethiopia ultramafic complexes are associated with enrichments in platinum-group elements ([Belete et al., 2000;](#page-18-0) [Selassie and Reimold, 2000](#page-18-0)). According to [Getaneh \(1985\),](#page-18-0) radioactive minerals are primarily deposited in Precambrian granites, Cretaceous, and Jurassic sediments of eastern Ethiopia. The geochemical data are used for different purposes such as mineral exploration, agricultural land management, environmental monitoring, etc. ([Appleton and](#page-18-0) [Ridgway, 1992; Plant et al., 2001](#page-18-0)). The geological setting of the Gimbi-Nejo area in west Ethiopia shows the high potential of economic minerals, but no comprehensive efforts have been made to evaluate the regional mineral potential due to warfare and the lack of transportation routes. The main aim of this regional multi-element geochemical prospecting is to use stream sediment and rock samples to explore the following: high potential ore-forming elements, new economic sites of mineralization associated with geological features, and anomalous zones for the focus of mineral exploration from multi-element geochemical mapping in the Gimbi-Nejo area, West Ethiopia.

2. Study area

Gimbi-Nejo (9100 km^2) is located in the western plateau of Ethiopia, between latitudes $9^{\circ}00'$ to $10^{\circ}00'$ N and longitudes $35^{\circ}15'$ to $36^{\circ}00'$ E (Fig. 1). Due to predominantly tropical highland and subtropical forest in the working area, the outcrops are in fair condition with various degrees of weathering. The stream sediments are the product of deposition of weathered rocks/minerals.

2.1. Geological setting

Gimbi-Nejo is considered the most representative exposed area of the Pan-African basements in west Ethiopia. Many previous works, such as [Kazmin \(1971, 1975\) Kazmin et al. \(1978\)](#page-18-0), [Gass \(1981\), Kroner \(1985\),](#page-18-0)

Fig. 2. Geological map of the Gimbi-Nejo area, West Ethiopia.

[Kroner et al. \(1991\), Shackleton \(1986, 1994\), Stern \(1994\), Ayalew and](#page-18-0) [Peccerillo \(1998\)](#page-18-0), [Woldemichael et al. \(2009\)](#page-19-0), [Williams \(2016\),](#page-19-0) and, [KHAN et al. \(2022\),](#page-19-0) suggest that west Ethiopia had experienced different stages of tectonic activities, which produced unique material records, deformation features, magmatism, and metamorphism. These geological settings indicate high ore potential. Several types of deposits are formed by different geological activities such as crystallization of magma, metamorphism, and weathering, etc. ([Arndt et al., 2017\)](#page-18-0).

The study area mainly consists of bedded metamorphic rocks with intrusive and extrusive igneous rock units ranging from the Precambrian to Tertiary. The field survey in combination with literature review (e.g., [Kazmin, 1971, 1975; Kazmin et al., 1978](#page-18-0); [Asrat et al., 2001; Williams,](#page-18-0) [2016;](#page-18-0) etc.) shows that Precambrian bedded metamorphic rocks, Paleozoic-Mesozoic sedimentary rocks, Tertiary volcanic rocks, Quaternary deposits, and Tulu Dimtu Tectonic mélange belt are well exposed. The bedded metamorphic rock and stratum comprised various gneisses, pyroclastic and metasedimentary, and meta mafic–ultramafic intrusive rocks that make up about 85 % of the base area. The intrusive rocks are also widely distributed. They vary from basic intrusive rocks,

intermediate basic intrusive rocks to intermediate acid intrusive rocks. All these western Ethiopian rock units have a good potential for mineralization [\(Belete et al., 2000; Mogessie and Belete, 2000;](#page-18-0) [Tadesse](#page-19-0) [et al., 2003](#page-19-0)). After a field survey based on different deformation patterns, metamorphism, volcanism, and sedimentation, the exposed rock units mentioned above are reclassified on a geological map for understanding the geological features related to mineralization (Fig. 2).

2.2. Drainage system

The stream system is relatively developed in the study area, particularly in Blue Nile and Baro. Regionally, rainfall is strong, but a few areas occasionally lack streams during the dry season. The lineation of most drainage patterns suggests that they are structurally controlled ([Fig. 3](#page-3-0)a). The stream is filled with angular to sub-rounded rock fragments, ranging from boulder to sand in size, while the fine sand, silt, and clay particles are interspersed in the debris.

Fig. 3. (A) Sample collection points are evenly distributed on the topographic map.(B) Each big grid cell is divided into four small sampling cell (C) Steps of working procedure after collecting samples in the field camps. Circles are sample points, blue lines are streams, and red dotted lines are drill sampling sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Methodology

The 1:250,000 scale geochemical survey in Gimbi-Nejo includes both outdoor work (field sampling) and in-door work (laboratory analysis). The outdoor work mainly involved sampling stream sediments from active drainage systems and rock samples from surrounding outcrops ([Ridgway et al., 2009\)](#page-19-0). Multi-methods and multi-instruments were adopted, following the procedure proposed by [Cheng et al. \(2014\)](#page-18-0) during laboratory work.

3.1. Field sampling procedure (Out-door work)

The field sampling was limited between September and December. The stream sediment samples were collected to detect geochemical signatures related to mineralization, while the rock sampling aimed to measure the trace element composition of the major geological units. This helped to determine the background and relative anomalous levels of the relevant elements in the stream sediment samples. The stream sediments, mainly sludge, siltstone, and sandstone at each site were collected from several points to produce − 20 mesh representative

composite samples. These samples were mainly collected with a trenching tool from first and second-order streams of 1 km long (Fig. 3). A total of 2254 composite samples weighing 220 g each were collected during the field work. The average sampling density is 2.33 samples per 4 km^2 (Fig. 3b). Similarly, 516 rock samples from surrounding outcrops weighing 300 g each were also collected during the field survey. Rock sampling sites were selected based on the lithological variation. The soil samples from undeveloped stream areas and different exploration methods like drill hole testing, trenches, etc., were also adopted to improve the accuracy.

After collection, samples were put into cloth bags with identifying numbers and then taken to the field camp for drying and sieving. Each sieved sample was homogenized, coned, and sub-sampled into two parts in the next step. One part weighing about 100 g was left in bottles for future reference, while the other 120 g was used for further analytical analysis (Fig. 3c). The GPS (eTrex, XL-12) coordinates (UTMzone.36) of each sample position were also recorded for future reference. Quality control during sample collection was to avoid contamination and deterioration [\(Johnson et al., 2018;](#page-18-0) [Ridgway et al., 2009;](#page-19-0) [Lapworth et al.,](#page-19-0) [2012\)](#page-19-0).

Showing the analytical methods with threshold and standard limit of each oreforming elements.

Elements	Methods	Threshold limit $(\mu g/g)$	Standard limit $(\mu g/g)$
Ag	ES	0.1	0.02
As	AFS	9.0	1
Au	FAES	0.0035	0.0003
B	ES	32.5	5
Ba	ICP-AES	760	50
Be	ICP-MS	2.15	0.5
Bi	AFS	0.25	0.1
Cd	ICP-MS	0.1	0.03
Co	$\sf{ICP\text{-}MS}$	60	1
Cr	XRF	500	15
Cu	XRF	70	1
$\rm F$	ISE	394	100
Hg	AFS	0.025	0.0005
La	ICP-MS	35.9	30
Li	ICP-MS	19.8	5
Mn	ICP-AES	2253	30
Mo	ICP-MS	2.0	0.4
Nb	XRF	42.5	5
Ni	ICP-MS	100	$\overline{2}$
P	XRF	1412	100
Pb	ICP-MS	16	$\overline{2}$
Pd	FAES	0.0025	0.0003
Pt	FAES	0.0015	0.0003
Rb	XRF	63.6	$\overline{}$
Sb	AFS	0.4	0.1
Sn	ES	3.0	1
Sr	ICP-AES	247	5
Th	ICP-MS	7.7	4
Ti	XRF	25,000	100
U	ICP-MS	$3.2\,$	0.5
V	ICP-AES	335	20
W	ICP-MS	2.5	0.5
Y	XRF	38.7	5
Zn	XRF	95	10
Zr	XRF	550	10
SiO ₂	XRF	755,000	0.1
Al_2O_3	XRF	197,000	0.05
Fe ₂ O ₃	XRF	188,000	0.05
MgO	ICP-AES	28,800	0.05
CaO	ICP-AES	35,000	0.05
Na ₂ O	ICP-AES	19,000	0.05
K_2O	XRF	28,000	0.05

Remark: Inductively coupled plasma-atomic emission spectrometry (ICP-AES), X-ray fluorescence spectrum (XRF), inductively coupled plasma mass spectrometry (ICP-MS), Atomic emission spectrometry (ES), Atomic fluorescence spectrometry (AFS), Ionic selection electrometry (ISE), Fire-assay emission spectrography (FAES).

3.2. Sample preparation and analyses (In-door work)

Analysis of soil, composite sediment, and rock samples were conducted in the Test and Monitoring Center of Wuhan (Geochemical Laboratory of China Geological Survey, CGS), the Ministry of Land and Resources China, and also in ALS Chemex (Guangzhou) Co., Ltd, China. All samples were analyzed for 42 selected elements: Cu, Pb, Cd, La, Li, Sn, Fe₂O₃, Mn, Co, P, U, Zr, Th, Rb, Nb, Sr, Ba, Pt, Pd, K₂O, Na₂O, CaO, MgO, V, Mo, Hg, Ni, Cr, Ti, W, Bi, Au, Sb, As, B, SiO2, Al2O3, Y, F, Be, Ag, Zn. A multi-method and multi-instrument analytical approach was adopted (Table 1). Analytical instruments include XRF, ICP-AES, and ICP-MS, and futher analytical techniques were used to evaluate elements with low crustal abundance. All samples including sediments, soil, and rock preparation were completed at the geochemical laboratories; before the samples were analyzed, about 80 g of each sample was dried at 110 ◦C in the oven then pulverized with a planetary ball mill to 0.074 mm (200 mesh) for the major and trace element analyses, rest sample for future reference.

An automated PANalytical Axios max XRF was used for above element analyses after 400 mg of each sample were pelletized. For the

detailed method description of XRF, refer to [Beckhoff et al. \(2006\)](#page-18-0) . A Thermo X Series-2 VG Elemental ICP-MS was used for element analyses; 250 mg of each sample was dissolved with a mixture of $HF + HNO₃ +$ $HClO₄$ + aqua regia by evaporating to dryness. In a 25 ml (5 %) aqua regia solution, the residue was dissolved. After pipetting, the clear upper solution was 10 ml diluted with $HNO₃(2%)$. The same procedure with a mixture of $HF + HCl + HNO₃ + H₂SO₄$ was used to analyze La. For the detailed preparation and analytical method description of ICP-MS, follow [Briggs \(2002\)](#page-18-0) and [Yao et al. \(2011\).](#page-19-0) An ICP-AES was used for element analyses; 250 mg of each sample was dissolved with a mixture of $HF + HNO₃ + HClO₄ + aqua regia by evaporating to dyness. In a 25$ ml (3 %) aqua regia solution, the residue was dissolved. The detailed method description of ICP-AES, can be found in [Thomas and William](#page-19-0) [\(1997\), Briggs \(2002\),](#page-19-0) [Yao et al. \(2011\)](#page-19-0) and [HU and YI \(2017\).](#page-18-0) The detailed method description of further analytical techniques AFS (2202E), ES, ISE, and FAES, are referred to [Ficklin \(1970\), Whitehead](#page-18-0) & [Heady \(1970\), Cooley et al. \(1976\),](#page-18-0) [Kuznetsova et al. \(2007\)](#page-19-0), Sánchez-Rodas et al. (2010), [Yao et al. \(2011\), Xiong et al. \(2011\)](#page-19-0).

China Geological survey set the standard limit for each element ([SPC,](#page-19-0) [2004\)](#page-19-0). The average content of each element was accepted after a 12 time repetition of each analytical process. The histogram of each exposed rock unit and number of Chinese standard reference samples for calibration during each analytical process with detection limit, percent of reported samples, and relative standard deviations (RSD) is present on each element's geochemical anomaly map. The element Au, Pt, and Pd were treated separately with China national geochemical standard reference samples: GBW-07288, GBW-07289, GBW-07290, GBW-07291, GBW-07292, and GBW-07293. The analytical methods with the threshold limit and standard limit of each ore-forming elements are shown in Table 1.

3.3. Quality control

The rigorous analytical quality control procedures were applied using Chinese standard reference samples and duplicate samples (both field and laboratory duplicate samples) to test the precision and accuracy of the methods ([Johnson et al., 2005, 2018;](#page-18-0) [Lapworth et al., 2012](#page-19-0)). A quality control (QC) program covered all features of the geochemical study, from collecting samples in the field to laboratory data analysis. The external quality control was conducted by the inspection unit of a regional geochemical sample analysis quality, China geological survey (CGS) at the end of each workday; field records were rechecked at the field camp to verify that every procedure was done correctly and samples were correctly handled until they were dispatched for laboratory analysis. The sample-site/field duplicate samples were randomly inserted into each batch of 10 samples, subsequently packed into cardboard boxes, and sent to the analytical laboratory in China.

During internal quality control, China national reference samples were simultaneously analyzed in the analytical blocks to appraise the accuracy of the methods. Twelve China national geochemical standard reference samples were inserted into each batch of 500 stream sediment samples. After analysis, the Logarithmic difference $(\triangle \lg C = |lg Ci - lgCs|)$ between measured and standard values was acceptable. In order to control the long-term stability of the methods, four monitoring samples (China national geochemical standard reference samples) were inserted into each batch of 50 stream sediment samples and were regularly analyzed. After analysis, the average log difference of the concentrations ($ΔlgC$) and the standard deviation (λ (GRD)) was found to be within acceptable standards for all elements. To check the reproducibility of the results statistically, replicate analysis was performed on 5 % of the total number of samples. After analysis, the relative difference (RD = 2×∣A1- A2|/|A1 + A2|×100 %) between basic and replicate analysis was also within the acceptable range for each element. The sample-site/field and laboratory duplicate samples were also analyzed to monitor the precision of the analytical methods and sampling error. One hundred nineteen duplicates were collected from the study area and analyzed with the

The degree of elemental differentiation in the Gimbi-Nejo area, west Ethiopia.

Differentiation degree	Uniform distribution	Relatively uniform distribution	Differentiation	Strong differentiation
CV interval Elements	${<}0.5$ $SiO2$, Al_2O_3 , Y, F, Be, Ag, Zn	$0.5 - 0.7$ Cu, Pb, Cd, La, Li, Sn, $Fe2O3$, Mn, Co, P, U	$0.7 - 1.0$ Zr, Th, Rb, Nb, Sr, Ba, Pt, Pd, $K2O$, Na ₂ O, CaO, MgO, V, Mo, Hg	>1.0 Ni, Cr, Ti, W, Bi, Au, Sb, As, в

Table 3

A geochemical anomalous zones contain ore-forming elements associated with geological features of the area.

Name	Elements/ Anomalies	Geological category	Name	Elements/ Anomalies	Geological category
HS1	Cu, Zn, Cd, V	I,V	HS17	Cu, Cr, Ni, Co, V	VI
HS ₂	W, Bi	III, V	HS18	Au, Ag, Cu, Ni, Sn, Mo	V.VI
HS3	Zn, V, Fe, Ni	П	HS19	Au, Cu, Pt, Pd	Ш
HS4	Pb, Mo, Sn, Bi	IV	HS20	Au, Pt, Pd, Cu, Ni	II,III
HS5	Cu, Ni, Pt, Pd	П	HS21	Au, As, Sb	Ш
HS ₆	Au, Pt, Pd, Cu, Ni	II, III	HS22	Ag, Hg, Ti	V
HS7	Au, Pt, Pd, Cu	I	HS23	Au, Pt, Pd	III, V
HS8	Zn, Cd	I	HS24	Au, Pt, Pd	II, III
HS9	W, Bi	I	HS25	Au, Pt, Pd, Cu, Ni	I
HS10	Au, Ag, W, Bi	Ш	HS26	Cu, Zn, Ni, Co, V	$_{\rm II}$
HS11	Au	V	HS27	Ag, Zn, Cd, Ti	V
HS12	Au, Pt, Pd, Cu	I	HS28	Cr, Ni, Co, Ag, Zn, Cd	$_{\rm II}$
HS13	Pb, W, Bi	IV	HS29	Pt, Pd	П
HS14	Ag, Pb, Mo, Zn	VI	HS30	Ag, Pb, W, Sn, Bi, Mo	V
HS15	Au, Ag, Mo, Bi	IV	HS31	Ag, Pb, Zn, Ni, Sn, Mo	VI
HS16	Au, Pt, Pd, Cu, Cr, Ni	П	HS32	Au, Ag, Zn, Pt, As, Sb	II, III, IV

HS; Geochemical anomalous zone.

Table 4

Remark: Unit for oxide is "%"; for Au, Ag, Hg, Cd is "ng/g"; & for other is "μg/g".

normal samples. Assay results of the duplicate samples were checked by plotting the absolute difference between the duplicates against the mean of the duplicates to calculate the relative error (RE% = $|A1-A2|/ (A1 +$ A2) * 100 %). It was also found that no significant differences existed between the analyses of the duplicate pairs, indicating good precision and accuracy levels. A relative error of RE% \leq 33.3 % was obtained which is negligible. In short, stream sediment samples in the project were consistent with the "standard" requirement, and they are reliable for geochemical mapping and interpretation ([Ye, 2002; Xie et al., 2003;](#page-19-0) [Ye and Yao, 2004](#page-19-0)).

4. Results

4.1. Analytical data

The trace-element concentrations of stream sediment samples are listed in Table 4. These data clearly suggest that about 15 elements have high economic potential with higher contents: Au (2.14 ng/g), Cu (43.56 μg/g), Cr (365.1 μg/g), Ni (69.2 μg/g), Co (34.46 μg/g), V (204.1 μg/g), Ti (13278 μg/g), Mn (1472 μg/g), Fe₂O₃ (10.97 %), P (888 μg/g), Al₂O₃(14.05 %), Ba (501.7 μ g/g), Zr (309.5 μ g/g), Sr (155.7 μ g/g) and Nb (28.2 μg/g). Results of rock samples shown in [Table 5](#page-6-0) are considered as background values of stream sediments.

4.2. Map compilation

According to elemental concentrations, geochemical anomaly maps of 42 elements and five composite geochemical anomaly maps were acquired using the MAPGIS 6.5 and GeoExpl 2005 softwares from a scanned copy of the topographic sheet NC36-8 (Gimbi) for data manipulation visualization and presentation (Figs. $4 \& 5$). The regional geological map was also generated to link anomalous levels of elements and geological units. Anomalous contours of elements suggest that in the study area, transitional metals enriched with high average contents relative to Chinese recommended values may be the focus of exploration in the migmatitic gneiss (Cu \sim 66.38 $\mu\text{g/g}$), granitic orthogneiss (Zr \sim 426.9 μg/g), upper basalt/lower basalt (Nb \sim 63.4 μg/g), meta-volcanic $(Mn \sim 2680 \mu g/g, Ti \sim 29823 \mu g/g, V \sim 365.6 \mu g/g, Fe₂O₃ \sim 16290000$ μg/g), meta-sedimentary formation (Au ~ 0.0053 μg/g), Abshala tectonic melange (Cr \sim 2457.1 μg/g), and meta-ultrabasic rocks (Co \sim 62.65 μg/g, Cu ~ 66.38 g/g, Ni ~ 313.4 μg/g). Consequently, it is interesting to establish 64 newly mineralized sites (31 Au, 16 Cu, 10 Ni

(*continued on next page*)

K. Junaid et al.		

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K. Junaid et al.		

Table 5 (*continued*)

Remark: Units for oxide is "%"; for Au, Pt, Pd, Ag, Hg, Cd is "ng/g"; & for other is " μ g/g".

Fig. 4. Composite geochemical anomalies map showing the distribution of Au-Ag-Pb-Zn-As-Sb-Hg-Cd concentration related to geological features of Gimbi-Nejo area with different geochemical anomalous zones (HS).

[Co-Cr], and 7 Fe) (Fig. 4). Further, the following anomalous zones, HS12, HS16, HS18, HS19, HS20, and HS28, could be of valuable mineral exploration.

5. Discussion

5.1. Distribution and variation of ore-forming elements

According to the distribution model test (multi-geo-spatial data management and analysis system GeoExpl 2005 program for calculation, [Yao et al., 2011](#page-19-0)), ore-forming elements in the study area essentially display normal or lognormal distribution. The histograms of each geological formation, which are shown on individual geochemical anomaly maps, suggest that the distribution of Ag, Pb, W, Sn, Be, Mo, La, Li, Sr, Th, U, Ti, F, P, Al2O3, Au, Pt, Pd, Ni, Ba, Nb, Rb, Sb, K2O are symmetrical; but these are negatively skewed for Cu, Zn, Cd, As, Hg, Y, Mn, Co, V, Bi, CaO, Na₂O, SiO₂, and inversely positively skewed for MgO. The distributions of B, Zr are bimodal, and Cr is multi-modal. [\(Ren](#page-19-0) [et al., 1993](#page-19-0)). The Chinese background statistical values of stream sediments were obtained from 1:200,000 scale geochemical sampling of 48 map sheets sharing similar geological settings with the studied area ([Table 4\)](#page-5-0). Based on these backgrounds, comparison with the average contents of elements in stream sediment samples collected from the

study area shows that transitional metals (Au, Cu, Cr, Ni, Co, V, Ti, Mn, $Fe₂O₃$, Zr, Nb), non-metal (P), alkaline earth elements (Ba, Sr), and basic metal $\text{(Al}_2\text{O}_3)$ in the study area are higher, while the contents of As, Sb, Bi, Hg, B, Be, W, Sn, La, Li, Th, Cd, Pb, F, Na₂O, and K₂O are lower. However, the most significant difference is represented by the values of Hg, Sb, and As contents in the area, which are two to three times lower than the recommended respective contents [\(Table 4](#page-5-0)). The low content of Hg, Sb, As, and high iron group elements distribution may be attributed to the extensive occurrence of basic-ultrabasic rocks within the Precambrian metamorphic terrane of the region.

The variation of elements concentration was measured by determining the coefficient of variation; $CV(%) = S/X*100$, where CV is coefficient of variation, S indicates standard deviation, and X is mean concentration. The coefficient of variation was utilized to evaluate the degree of elemental differentiation in the Gimbi-Nejo area ([Table 2\)](#page-5-0). The main types of element differentiation related to the major geological processes that were active in the area, including enrichment of Au, As, B, Bi by *meta*-volcanic and sedimentation; syngenetic enrichment of Cu, Pt, Pd, Cr, Ni, V, Ti, etc. by basic-ultrabasic magmatic events; dilution of Hg, Bi, As, Sb, etc. concentrations by metamorphism; and enrichment of Au, As, Sb, Hg, etc. as the result of hydrothermal activities. The enrichment of the main ore-forming elements and their associated components in the study area are related to locations of intense differentiation, which

Fig. 5. Geochemical map showing the distribution of "Ti" concentration in the Gimbi-Nejo area, West Ethiopia.

are thus the focus of exploration.

5.2. Ore-forming element enrichments in geological formations

Ore-forming elements are enriched in the Precambrian to Tertiary exposed rocks in the study area. The average contents, coefficient of variation, and enrichment factor of all considered elements in each stratigraphic unit are shown in [Table 5](#page-6-0). This regional geochemical information introduces new geochemical backgrounds for Ethiopia's most common geological domains. The analysis of each geological formation hosting chalcophile, siderophile, and lithophile elements are shown in five composite geochemical maps and are briefly descripted below.

5.2.1. Metamorphosed intrusive rock units

Migmatitic gneiss (Pmbhgn) and Granitic orthogneiss (Pgtgn) are two Precambrian metamorphosed intrusive rocks in the study area ([Fig. 2](#page-2-0)). In the Pmbhgn, strong differentiation of Au As, B, Cr, Ni (\geq 1.0) indicates that partial enrichments are due to later superimposed hydrothermal activities and intermediate to basic components of the intrusion. In the Pgtgn, strong differentiation of the high background

elements (Pd, Ag, Th, U, La, F, Y, Be, P, Ti, Hg, $SiO₂$) also suggests the superposition of late hydrothermal activities as the essential cause of the local geochemical anomalies [\(Fig. 4](#page-9-0)).

5.2.2. Precambrian aba sina domain

In this domain, Sayi Chenga volcanic-sedimentary formation (Psmv) is distributed on the north–south trending zone on the east side of the Belete shear zone. The Psmv is characterized by enrichment of MgO, Na2O, and CaO with high average contents of Au, Zn, As, Sb, B, Cd, Cu, Pt, Pd, Cr, Ni, Co, W, Sn, and low contents of Zr, Y, Nb, Rb, U, La, Th. The strong differentiation of Au, As, Sb, and B suggests the superposition of syn. to late hydrothermal activities. The composite anomalies of Au, Zn, As, and Sb appear here as the indicator of mineralization ([Fig. 4\)](#page-9-0).

5.2.3. Precambrian Chochi domain

The Precambrian Chochi domain consists of gneiss (Pbhgn) and pelitic-arenaceous schists (Ppsch). Pbhgn is located in the central north side of the work area with poor abundances of Au, As, Sb, Hg, associated with siderophile elements, rare earth and radioactive elements, high background - enrichment of CaO, Na2O, K2O, SiO2, MgO, Ba, Rb, Sr, Bi

A geochemical anomalous zone HS16 contains dominant elements characteristic values.

Element	Au	Pt	Pd	Cu	Ag	Zn	As	Sb	Ni	Co	Cr
Area (km^2)	40	76	48	92	32	52	36	32	80	24	96
Shape	zonal	oval	oval	zonal	oval	oval	oval	irregular	zonal	oval	oval
Maximum value	13.6	8.2	6.9	145.9	212.0	228.1	23.1	1.64	716.9	103.5	12,912
Average value	6.44	2.66	4.2	89.1	144.0	138.9	15.8	0.82	252.3	80.1	2522
Contrast	1.84	1.77	1.68	1.27	1.44	1.46	1.76	2.05	2.52	1.34	5.05
Dimensions	73.6	134.5	80.6	116.8	46.1	75.9	63.4	65.6	201.6	32.16	484.8

Remark: Units for Au, Pt, Pd, Ag is "ng/g"; & for other is "μg/g".

and weak enrichment of W. The coefficient of variation of Bi (3.12 %) and W (1.69 %) in Pbhgn is indicative of strongly non-uniformal distribution. There are superpositions of medium–high temperature hydrothermal activities as a cause of partial W & Bi anomalies. The strong differentiation of Au, As, B, Cr, and Ni suggests the superposition of local hydrothermal activities and the late intrusion with intermediate-basic components. Ppsch has distributed within Chochi and Digiro river with poor contents of Au, Hg, Cr, Ni, Ti, Pt, Pd and enriched contents of Ba, Th, Rb, Sr, Li, U, W, Pb, B, Na₂O, and K₂O. In the Chochi domain, all anomalies suggest the superposition of magmatic-hydrothermal mineralization-related activities ([Fig. 4\)](#page-9-0).

5.2.4. Precambrian Kata domain

The Precambrian Kata domain contains *meta*-volcanic (Pamv) and *meta*-sedimentary formation (Pams) of the

Aleltu group and Guliso formation (Pgl) of the Bila group. Pamv is distributed in the Chochi shear zone in the northwest of the working area. The statistical results of samples show the high contents of W, Zn, Mn, V, Ti, $Fe₂O₃$ and the most deficient contents of Pb, La, Nb, Be, Rb, K2O in the whole domain [\(Tadesse et al., 2003\)](#page-19-0). According to the degree of elemental differentiation, the coefficient of variation of Ag, Cu, and Zn is *<*0.5 μg/g, showing uniform distribution. The strong differentiation of Au, As, Pt, Pd, W, and Bi reflects the superposition of hydrothermal activities. The Pams is located west of the Belete shear zone and south of the Chochi shear zone. Strong differentiation of W, Bi, Ba, and Cr in this formation also suggests hydrothermal activities. The partial anomalies of W, Sn, Bi, and Mo reflect the effect of late superposition by the acidic component intrusion. The Pgl is one of the most critical formations for Au enrichment. Its elements differentiations of Cr, Ni, Pt, and Pd also reflect the late superimposed intrusion of intermediate-basic components in Pgl [\(Fig. 4](#page-9-0)).

5.2.5. Meta-basic to ultra-basic rocks

This rock unit was composed of Abshala tectonic melange (Paml) and meta-ultrabasic rocks (Pumf). The Paml is distributed in Belete NStrending shear zone with strong differentiation of Au, As, B, Sb, Cr, Ni, Co, Pt, and Pd reflecting superimposed enrichment of the late hydrothermal mineralization events. Au displays an enrichment trend with the metabasic - ultrabasic component in the same period. The Pumf is also distributed in the Belete NS-trending shear zone with strong Au, As, and Sb differentiation, reflecting superimposed hydrothermal mineralization events. Au has the ore-forming tendency to accompany Pt, Cu, Cr & Ni in rock units. The differentiation of Sn with low content reflects the superposition of the late hydrothermal activity [\(Fig. 4](#page-9-0)).

5.2.6. Metagabbro-amphibolite and gabbroic complex (Pgb1/Pgb2)

The basic intrusive rocks in the work area were previously divided into metagabbro-amphibolite (Pgb1) and annular gabbroic complex rock (Pgb2). These are mainly-three parallel zonal distributions with the north–south direction of the Tulu Dimtu structural zone. The strong differentiation of Cr and Ni indicates enrichment of late superimposed hydrothermal events. The Au coefficient of variation reaches up to 1.6 %, showing strongly non-uniformal distribution, associated with strong

differentiation elements (As, Sb $\&$ B), suggesting the superimposed mineralization of the late low-temperature hydrothermal activity ([Fig. 4\)](#page-9-0).

5.2.7. Intermediate-basic (Pdt &Pgb) and acidic intrusive rocks (Pgt3 & Pgt2)

The intermediate-basic intrusive rocks are distributed in the Dengi litho-tectonic domain to the west of Belete NS trend shear zone and south of Chochi NW trend shear zone, covering an exposed area of 1604 km². Statistical data show that Au, Cr, Pd, B, Ti, and Sb have strong differentiation. The Au coefficient of variation reaches up to 2.18 ng/g. Its distribution is uneven, indicating mineralization by the late tectonic hydrothermal activity in the Chochi shear zone. It leads to Au enrichment by hydrothermal migration within intermediate-mafic intrusive rocks in the vicinity of the shear zones and southwest side of Chochi shear zone.

The Pgt3 & Pgt2 rocks are widely spread in the work area of 928 km^2 . The enriched elements W, Sn, Be, Bi, Ba, Rb, Th, U, SiO₂, Na₂O, and K₂O were essentially of granite characteristics. The strong differentiation of Au, As, Hg, B, W, Bi, Mo, Th, Nb, Cr, Ni, Co, V, and Ti indicate superimposed enrichment related to magmatic-hydrothermal mineralization activities, which leads to the Zr, La, Nb, Rb, Yu, Th series, and W, Sn, Bi, Mo series covering a large area of granite. In the acidic rocks, local fractionation and concentration of Cr, Ni, Co, V, Ti, and siderophile elements may also suggest the presence of superimposed basic-ultrabasic intrusion ([Fig. 4\)](#page-9-0).

5.2.8. Tertiary volcanic rocks

These rocks with multi-element enrichment are distributed in the southwest and northeast of the work area (1384 km^2) . In this lithologic unit, strong differentiation of Au and B indicates the superimposition of partial weak mineralization ([Fig. 4](#page-9-0)); apart from that, other high background elements (Ag, Zn, Pb, Hg, and Cd) are uniformly distributed. In such case of no significant differentiation, mineralization is limited to *syn*-magmatism, and the late superimposed hydrothermal mineralization is not significant.

5.3. Characteristic of geochemical anomalous zones

The studied areas in Gimbi-Nejo can be further divided into thirtytwo distinct anomalous zones (HS) based on dimension, intensity, geological environment, and spatial association of the ore-forming elements. Each zone is characterized by several dominant ore-forming elements [\(Table 3](#page-5-0)). The statistical values suggest that distribution of these elements are associated principally with the following geological features: tectonic hydrothermal activities (I), meta*-*basic and metaultrabasic rocks (II), metamorphosed volcanic and sedimentary rocks (III), intermediate-acid intrusive rocks (IV), intermediate-mafic intrusive rocks (V), and Tertiary volcanic lava (VI) ([Table 3\)](#page-5-0). In the study area, most important anomalous zones are HS5, HS12, HS16, HS19, HS21, and HS28 for the vital inspection, while HS11, HS18 HS20, HS25, and HS32 are for reconnaissance inspection. The primary anomalous zone typically contains strong serpentinization, talcization, and

Fig. 6. Geochemical anomalous zone map of HS16 showing composite anomalies of Au, Cu, Pt, Pd, Cr, and Ni.

silicification in meta*-*ultrabasic rocks with nickel, platinum, and chromium enrichments. Some anomalous zones have sulfide-bearing quartz veins controlled by a northwest-trending shear zone with high gold and copper mineral potentials. In the HS20 anomalous zone, nickel, gold, and cobalt mineralization were found in Tulu Dimtu.

Most importantly, the geochemical anomalous zone HS16 contains Au, Pt, Pd, Cu, Cr, and Ni composite anomalies ([Table 6](#page-11-0), [Fig. 4\)](#page-9-0). This likely specific zone is located in the Hagelo meti area at the centernorthern section of the Belete shear zone, between latitudes 9◦32′ ~9◦42′ N and longitudes 35◦45′ ~35◦51′ E. It consists of Abshala tectonic mélange, meta-ultrabasic rocks, meta-gabbro amphibolite, Sayi chenga volcanic-sedimentary rocks, siltstone interbedded with claystone and shale (Luma), schistositized medium-grained quartz monzonite-monzonite, and trachyte lava (Fig. 6). These rocks well developed serpentinization, steatitization, chloritization, contain quartz veinlets in the fissures, and are weakly mineralized. In fact, several types of ore sites can be determined in the HS16, including two placer gold ore spots, one nickel (cobalt) mineralized spot, two mineralized nickel spots, and two talc mineralized spots. In considering the mineralization associations in the zone (HS16), two composite anomalous series, Cu-Pt-Pd-Cr-Ni-Co-V and Au-Ag-As-Sb-Cd, can be distinguished in the northwest direction about 15 km in length and 12 km in width. Au, Pt, Pd, and Cu anomalies are closely coexisting in zone, and the peak values are up to13.6 ng/g, 8.2 ng/g, 6.9 ng/g, and 145.9 μg/g, respectively. The ovalcontoured Ag, As, and Sb anomalies partly overlapped within the north and south ends of the zone, while Cr, Ni, and Co anomalies are completely overlapped. The results of the 1:50,000 scale stream sediment survey show that Au, Cu, Pt, and Pd anomalies have good reproducibility, and the intensity is significantly increased in HS16. These anomalies are contoured 5 km^2 northern and 11 km^2 southern by the threshold limit respectively 5.0 ng/g, 100 μg/g, 3.5 ng/g, and 8.0 ng/g ([Fig. 7](#page-13-0)). The maximum contents of Au, Cu, Pt, Pd, Cr, and Ni in this zone are 15.0 ng/g, 186.1 μg/g, 11.4 ng/g, 24.7 ng/g, 79739.2 μg/g, and 1819.0 μg/g ([Table 6\)](#page-11-0). According to the data from the 1:10,000 scale soil

profile, it can be seen that there is intense Pt, Pd, Cr, and Ni mineralization showing in altered rocks (Pumf), the peak values of Pt, Pd, Cr, and Ni, respectively are 10.8 ng/g, 20.7 ng/g, 13627 μg/g, and 2473 μg/g ([Fig. 8](#page-14-0)). The obtained geochemical mapping data of the whole study area suggest that the anomalous zones, HS12, HS16, HS18, HS19, HS20, and HS28, could be the favorable focus of exploration. Based on our geochemical mapping results, one Chinese mineral company (Mindi mining PLC) has started working in an anomalous zone (HS28) to explore Ni and Co.

5.4. Excavation testing

In order to ensure the accurate information of ore-forming elements in stream sediments, multiple exploration methods, including geological traverse section, exploratory trenches, shallow shaft, drill hole testing, etc., were adopted, and *>*60 mineral deposits have been found. The mineral separation has been conducted in the high anomalous zones like HS12, HS16, HS18, HS19, HS20, and HS28. The anomalous zone HS19 is predominant in the study area due to the enrichment of Au, Cu, Pt, and Pd [\(Fig. 4\)](#page-9-0). In HS19, panning activity is a typical scene in all scales of streams for mineral separation. The placer gold has two sources in HS19, either directly collected from the river channel, or collected by digging the lower part of the gravel stratum near the river channel ([Fig. 11](#page-15-0)c,d). In the Kata area along the HS19, there exists an adit at 0779733N/ 1049411E, approximately 150 m long. An Au-Cu-bearing quartz vein is on the wall at the entrance with solid carbonation, silicification, chloritization, and epidotization [\(Fig. 12](#page-16-0)). The highest Au (S-044-01) value up to 949 ng/g is obtained at the adit entrance ([Fig. 10](#page-15-0)). Due to strong weathering, a sampling section has been excavated 30 m away from the adit entrance. The analytical results are shown in [Table 7.](#page-17-0) In Giba Buraso area along the same HS19, auriferous quartz veins (length 2 km, width 3–15 m) intercalate felsic schist, and sericite-quartz schist has also developed in the N–S direction, with regional schistosity [\(Fig. 11](#page-15-0)a, b). The excavation has been done at 0783636E/1047828N to expose the

Fig. 7. Geochemical anomalous zone map of HS16 showing geochemical prospecting significance.

Fig. 8. Soil profile of composite anomalies of the geochemical anomalous zone (HS16).

6. Carbonic (graphite) sericite-quartz schist 7. Quaternary cover 8. Quartz vein 9. Pyritic quartz vein 10. Quartz vein with pyritization, chalcopyritization 11. Schistosity attitude 12. Sampling position and id 13. Layering position and id

Fig. 9. Sampling profile of BT2 excavation of geochemical anomalous zone (HS19).

Fig. 10. Sampling profile of adit PD1 of the geochemical anomalous zone (HS19).

Fig. 11. (A) Auriferous quartz vein zone, (B) Outcrop of weathered quartz veins extended in SE direction of BT2, (C) Panning pit on the flooded land of Kata river, (D) Panning activity for placer gold along stream channels.

Fig. 12. Adit for exploration minerals, (A) Gold-bearing quartz vein, (B) Visible gold in quartz vein, (C) Ore deposit contains pyrite and chalcopyrite.

vein system for sampling ([Fig. 9\)](#page-14-0). The results present in [Table 7](#page-17-0) yield the highest Au value of 1.43 ng/g. A traverse survey has also been conducted along the strike of auriferous quartz veins (BT2) to pursue their strike extension. Two grab samples (S-415-02 and S-415-04) were also gathered from weathered quartz veins, located southeast of BT2 (0783522E/ 1048334N; 0783441E/1049549N), getting Au values of 0.45 ng/g, 0.14 ng/g, respectively, indicating that auriferous quartz veins extend along the strike and show better gold mineralization ([Fig. 11a](#page-15-0),b). The primary mineralization in the quartz veins was pyrite and chalcopyrite (Fig. 12c). During the microscopice study of core samples, it can be seen that natural gold is filled in the pyrite micropores or mineral gaps ([Fig. 13](#page-17-0)), and gold is mostly irregular shaped or granular. The gold particles are about 1 μ m ~ 300 μ m, with an average of 11 μ m and bright gold is partially visible in the core samples. Same as in other highintensity values anomalous zone, excavation was done to know the surface extension of ore bodies and drilling at well-mineralized segments.

5.5. Spatial distribution

Geochemical anomaly maps are the main results of the geochemical prospecting. The major ore-forming elements in the research region include Au, Cu, Cr, Ni, Co, V, Ti, Mn, $Fe₂O₃$, P, Ba, Zr, Sr, Nb, Al $₂O₃$, and</sub> the associated elements are Pb, Cd, La, Li, Sn, U, Th, Rb, Pt, Pd, K2O, Na₂O, CaO, MgO, Mo, Hg, W, Bi, Sb, As, B, SiO₂, Y, F, Be, Ag, and Zn. Analytical data generate geochemical maps of each ore-forming element to show the possible anomalies and figure out the dispersion haloes. In the geochemical maps, anomalies were delineated based on 85 %, 95 %, and 98.5 % of the cumulative frequency distribution and designated as outer, middle, and inner anomalous zones. The uniform anomaly

threshold in the region was the content corresponding to the 85 % value of the cumulative frequency. These geochemical maps suggest that in the study area, mostly transition metals with high whole area average content as compared to Chinese recommended stream sediments values have high economic potentials and are mainly distributed in migmatitic gneiss (Cu ~ 66.38 μg/g), granitic orthogneiss (Zr ~ 426.9 μg/g), upper basalt/lower basalt(Nb \sim 63.4 μg/g) rocks, meta-basic (Mn \sim 2680 μg/ g, Ti ~ 29823 μg/g, V ~ 365.6 μg/g, Fe₂O₃ ~ 16290000 μg/g) rocks, meta-sedimentary formation (Au \sim 0.0053 μg/g), Abshala tectonic melange (Cr \sim 2457.1 μ g/g), and meta-ultrabasic rocks (Co \sim 62.65 μ g/ g, Cu ~ 66.38 μg/g, Ni ~ 313.4 μg/g). The composite maps of oreforming elements were also generated to represent the absolute concentration of ore forming elements in each rock unit with anomalous geochemical zone (HS) elements [\(Table 3](#page-5-0)) associated with geological features [\(Fig. 4](#page-9-0)). The obtained data of geochemical prospecting indicates 64 new mineralized spots in the study area, including 31 Au, 16 Cu, 10 Ni (Co-Cr), and 7 Fe. During geological field work also marked some new non-metallic minerals spots including talc, marble, cryolite, barite, lignite, etc. All these mineralized spots are present in composite maps ([Fig. 4\)](#page-9-0). Further studies are strongly recommended to raise the degree of essential geological and mineral resource exploration in west Ethiopia.

6. Conclusions

1. The present geochemical prospecting was conducted for forty-two ore-forming elements in a 9100 km2 area of the Gimbi-Nejo in west Ethiopia. After strict data monitoring, geochemical anomaly maps of stream sediments were generated, which shows the possible anomalies of interested elements and explain their dispersion haloes. The composite maps of ore-forming elements were also established

A geochemical assay results of samples taken from excavation.

Remark: Unit is "μg/g"; Py: pyrite, Cpy: chalcopyrite.

Fig. 13. (A) Core sample bearing quartz vein, (B) Drilling samples of ore deposits, (C) & (D) Microscopic image showing pyrite mineral containing gold in the cavity.

to represent the absolute concentration of ore-forming elements in each lithologic unit.

- 2. The ore-forming element-enriched areas are divided into thirty-two distinct composite anomalous zones (HS). Among them, HS12, HS16, HS18, HS19, HS20, and HS28 could be the favorable focus of exploration due to intense differentiation.
- 3. In the study area, SiO_2 , Al_2O_3 , Y, F, Be, Ag, and Zn with coefficient of variation <0.5 were identified as uniform distribution; elements with coefficient of variation $0.5 \sim 0.7$, such as Cu, Pb, Cd, La, Li, Sn, $Fe₂O₃$, Mn, Co, P, and U, display relatively uniform distribution pattern; Zr, Th, Rb, Nb, Sr, Ba, Pt, Pd, K₂O, Na₂O, CaO, MgO, V, Mo, and Hg with coefficient of variation $0.7 \sim 1.0$ were considered as differentiation; Ni, Cr, Ti, W, Bi, Au, Sb, As, and B elements with coefficient of variation ≥ 1.0 were identified as strong differentiation within the ore-forming minerals. The obtained geochemical mapping indicates strong anomalies and thus high economic potentials for Au (2.14 ng/g), Cu (43.56 μg/g), Cr (365.1 μg/g), Ni (69.2 μg/g), Co (34.46 μg/g), V (204.1 μg/g), Ti (13278 μg/g), Mn (1472 μg/g), Fe₂O₃ (10.97 %), P (888 μg/g), Al₂O₃ (14.05 %), Ba (501.7 μg/g), Zr (309.5 μ g/g), Sr (155.7 μ g/g), and Nb (28.2 μ g/g).
- 4. According to the regional geological setting of the area, composite geochemical maps suggest that the intermediate-acidic and basic intrusive rocks, meta-sedimentary rocks, meta-basic, and metaultrabasic rocks, tertiary volcanic lava, and tectonic hydrothermal activities along the north–south structural belt have the dominant controlling role for regional mineralization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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