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Identifying geochemical anomalies associated with Sn-W mineralization using statistical methods in the Dong Van region, northeastern Vietnam

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Abstract

The Dong Van region is a prospective area for Sn-W mineralization in northeastern Vietnam. Statistical studies, including the mean ± 3 standard deviation (mean ± 3 STD), were used to identify geochemical anomalies for mineralizing elements and element associations. To examine polymetallic mineralization and thereby uncover polymetallic ore occurrences in this research location, 890 geochemical samples were employed. Furthermore, statistical and multivariate analysis aid in the identification of geochemical abnormalities in particular Northeastern areas. According to the statistical approach and cluster analysis of geochemical data, the Sn and W elements are good indicators, and most of them follow the geometric distribution. Based on the third-order threshold, the geochemical anomalies of the content of the Sn and W elements demonstrate the concentration of tin creating hidden ore bodies in the mineralized zone and clearly illustrate the concentration in separate zones. These findings suggest that the models may investigate geochemical anomalies and analyze the concentration trend of indicator elements in the Dong Van region. Furthermore, the statistical analysis suggests exploiting the region's bottom river sediments to examine polymetallic mineralization is a wonderful idea. Furthermore, geochemical data may be used to assess pathfinder element geochemical anomalies and possible mineral mapping in the Dong Van region of Northeast Vietnam.

Keywords

geochemical anomalies, Sn-W mineralization, statistical methods, Dong Van region, northeastern Vietnam

For citation

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1. Introduction

Mineral resource research relies heavily on stream sediment surveys, and numerous types of deposits have been identified in northeastern Vietnam [1, 2]. However, processing such data to find multivariate geochemical patterns and signals linked to mineralization [3]. The principal component analysis is a useful data analysis technique for reducing the number of variables in a dataset or identifying components that reveal hidden patterns in multivariate data [4, 5]. In addition to basic principal component analysis, the literature has several other types of principal component analysis [6, 7]. These methods may be used with raw data, log-transformed data, selected data, and other types of data [8].

Traditional statistical analysis tools such as probability graphs, univariate and multivariate analysis methods [8–10], and fractal and multifractal models such as number size have all been proposed to differentiate geochemical anomalies from background [11–14]. Reimann et al. [15] compared various statistical methods for determining element concentration threshold values. They found that the boxplot, median ± 2 median absolute deviations, and empirical cumulative distribution functions are better than the

mean ± 2 standard deviations for estimating anomaly threshold values. Fractal and multifractal algorithms have been frequently used to find geochemical anomalies due to the spatial autocorrelation nature of the data [16–18].

The Dong Van area in northeastern Vietnam is regarded as a significant location that has piqued geologists' interest as a prospective source of polymetallic ore (i.e., Fe, Mn, Sn, W, and Au) [1]. Furthermore, because tin, tungsten, and gold are commonly found combined in arsenic mineralization such as the As-Sn-W-Au Nam Khi, Lang Xum, Lang Me, and Lang Lup deposits, it plays an important role in supplying precious metals to industry [19, 20]. From 1965 until the present, this region has been surveyed at a scale of 1:500,000–1:50,000 for geological mapping and mineral exploration [21–24]. However, geological sample collecting and geochemical data processing are insufficiently represented and satisfied to establish that prospective Sn, W mineralization locations may be identified. As a result, it is critical to conduct more research in the Dong Van region of northeastern Vietnam in order to identify new polymetallic ore discoveries.

The statistic and multivariate analysis are used to explore 890 geochemical samples that allow for the prospecting of polymetallic mineralization in the Dong Van region of northeast Vietnam to find new polymetallic ore occurrences.

2. Geological settings

Within the northeast block of the Vietnam's segment is the Song Hien zone, a 200 kilometer-long NW-SE trending tectonic zone that formed the Song Hien formation's Permian-Triassic and Triassic volcanic-sedimentary sequences with subordinate middle-late Paleozoic terrigenous-carbonate rocks (Fig. 1). The Song Hien zone is thought to be either a late Paleozoic - early Mesozoic intracontinental rift basin related to the Emeishan plume [25–28] or a late Paleozoic - early Mesozoic back-arc basin formed by rifting of the amalgamated Indochina - South China plate caused by the accretion of the Sibumasu plate to it [29].

The study area belongs to the Song Hien zone of Northeast Vietnam (Fig. 1A). The lithology of the Dong Van region comprises mostly of Triassic sedimentary rocks (marlaceous shale, oolitic limestone, siltstone, tuffaceous sandstone, shale, sandstone), with Devonian, Carboniferous, and Permian sedimentary rocks (i.e., conglomerate, clay shale, carbonate rocks, and marly sandstone), Cambrian, and Ordovician sedimentary rocks also present in the Song Hien margin; Triassic gabbros, and undating granitoid rocks are distributed in the central and western part of the area [22–24, Fig. 1B]. Quaternary sediments are mostly found along valleys (i.e., sandstone and gravestones). The Dong Van region is located in the north part of the Song Hien zone extending northwest to southeast (Fig. 1B). The Cao Bang-Lang Son-Tien Yen strike-slip fault zone in the northern part and the Duong Thuong-Du Gia reverse fault in the southern part play an important

role in controlling the Song Hien structural zone [21]. The intrusive magmatic rocks in this area have been considerably driven by these faults and other minor fault systems, contributing to the area's more intricate structure [23].

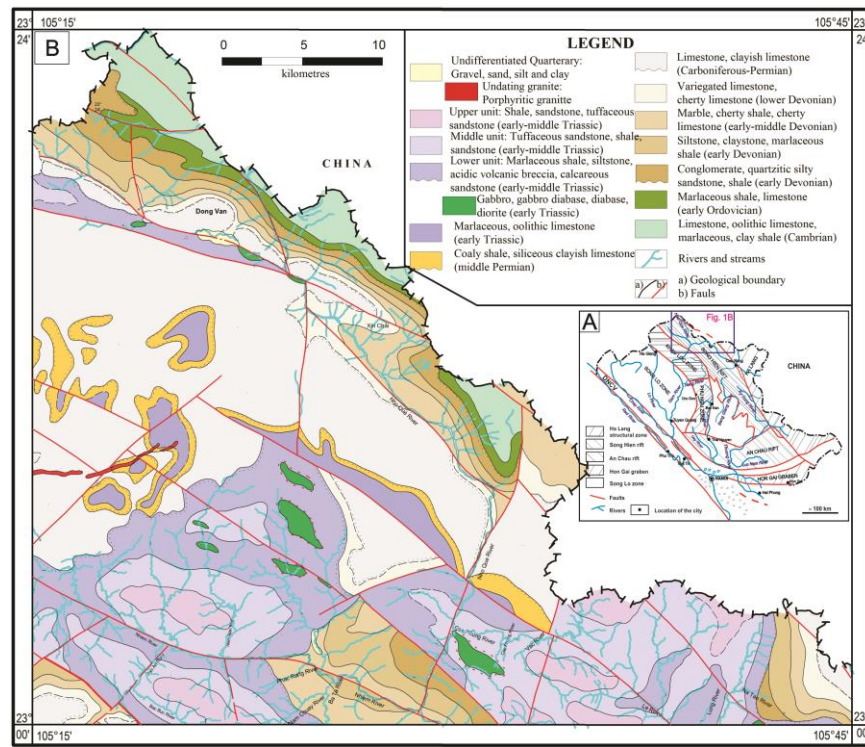


Fig. 1. Tectonic sketch map of northeastern Vietnam, showing the study area (A) [21]; Simplified geological map of the Dong Van region (B) (modified from [23])

There is a main polymetallic mineralization zone in the studied area, namely Dong Van, that last from the Northwest to Southeast with an area of 1,190 square kilometers and are mainly encompassed by Triassic sedimentary rocks [22–24, Fig. 1B]. According to [Truyen et al.](#) [23], uneven concentrations of Sn, W, and As were found in this mineralized zone, which is illustrated obviously by [Thang et al.](#) [30].

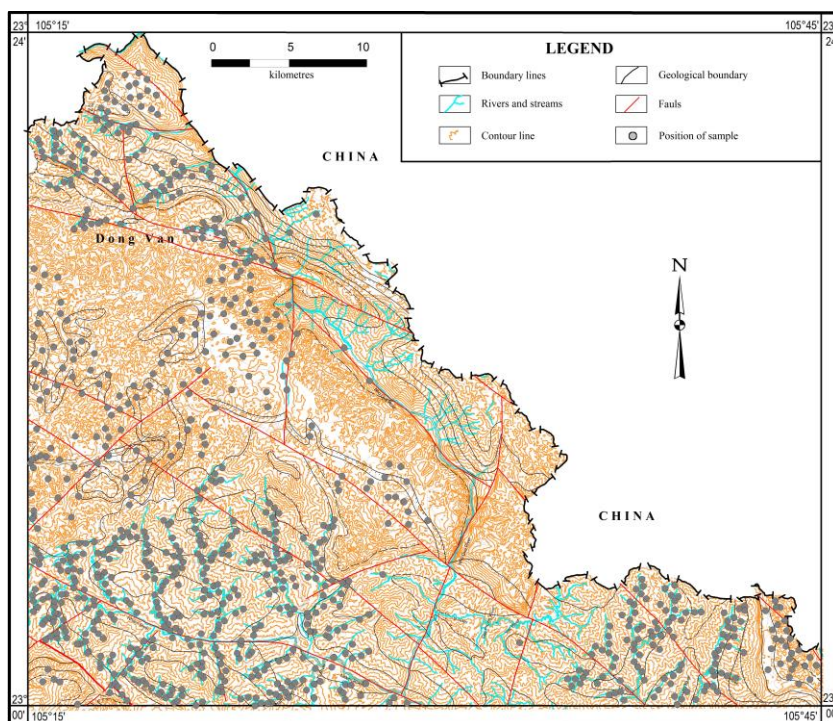


Fig. 2. General map of the Dong Van region, northeastern Vietnam, with bottom sediment sample sites (shown as black dots)

3. Materials and methodologies

3.1. Collection and preparation of bottom sediment samples

Geochemical exploration techniques for exploring mineral deposits usually use bottom sediment samples. For this investigation, eight hundred ninety geochemical samples of recent bottom sediments were collected along the river and streamlines at 25–50 m intervals. Surface sediment (0–3 cm depth) is collected as sub-samples with a flat hand shovel from all sites (about 50–100 m on both riversides) with low current velocities to retrieve fine and recent material. Each sample contains around 25–130 g of recent bottom sediment, depending on the particle size of the sediment sample (Fig. 2).

The sample sets were processed based on distinct characterizations of the zone's bottom sediments. In addition, the concentrations of 27 chemical components were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (i.e., Ag, As, Be, Ba, Bi, Cd, Ce, Co, Cr, Cu, Ga, Ge, La, Li, Mo, Nb, Ni, Pb, Sb, Sc, Sn, Sr, Ta, V, W, Y, and Zn).

3.2. Data transformation

In this study, a total of variable elements (i.e., Ag, As, Be, Ba, Bi, Cd, Ce, Co, Cr, Cu, Ga, Ge, La, Li, Mo, Nb, Ni, Pb, Sb, Sc, Sn, Sr, Ta, V, W, Y, and Zn) in the bottom sediment samples are processed. If the variables do not have asymmetric distribution, skewness (statistical distribution test) and transformed variables are used to assess the normal distribution of each variable [31]. Furthermore, ten distribution

models (geometric, special discrete, uniform, triangular, Pareto, binomial, exponential, lognormal, and gamma transformations) were also carried out to achieve normality and transition for the skewed variables [8, 32–34].

3.3. Multivariate Analysis

Multivariate analysis methods are used to clarify and explain correlations between multiple factors linked with statistical data throughout the assessment and collecting of this data.

Geostatistic 9.0 is used to examine the findings of correlation coefficients and cluster studies, which assist in analyzing links between elements and element groupings.

Cluster analysis aims to reduce the number of significant subgroups of people or things in an extensive data collection. The split is done based on the items' similarity across predetermined characteristics.

Ward (1963) describes Ward's mathematical technique as a criterion for studying hierarchical clusters. Ward [35] introduced a universal agglomerative hierarchical clustering technique, in which the criteria for picking the pair of clusters to join at each level are based on the optimal value of an objective function.

Eigenvalues and eigenvectors are used to express covariance and correlation coefficient matrices generally. Varimax rotation was performed in the meanwhile to enhance the factor loads. Ward's approach was used to do Pearson's correlation coefficients cluster analysis (or hierarchical cluster analysis), and the results are shown in a dendrogram.

4. Results and discussion

4.1. The characteristics of statistical distribution elements

The statistical distribution models of polymetallic ores and related elements can be used to identify the laws of their statistical distribution. Geochemical data for the entire region is displayed separately thanks to statistical analysis. As a result, the element concentrations in the whole region are $Pb > As > Bi > Li > Sn > W > Ta > Ce > Ag > Sb > Be > Mo > La > Nb > Cr > Ni > Cd > Y > Cu > Ba > Co > Sc > Zn > Sr > V$ (Table 1). Moreover, Pb, As, Bi, Li, Sn, W, Ta, Ce, Ag, Sb, and Be elements make up more than 90% of the total, indicating an obvious relationship with polymetallic ore. As a result, these elements might be used as indicators when prospecting for polymetallic mineralization.

Table 1. Frequency analysis of the content of the elements [ppm] for the sediment samples

Element	Amount of Information (AI)	Information combination (IC)	Probability (%)	Element	Amount of Information (AI)	Information combination (IC)	Probability (%)
Pb	0.573	0.573	30.02	Nb	0.337	1.842	96.49
As	0.572	0.810	42.41	Cr	0.313	1.868	97.87

Bi	0.564	0.987	51.69	Ni	0.235	1.883	98.64
Li	0.561	1.135	59.46	Cd	0.197	1.893	99.18
Sn	0.546	1.260	65.98	Y	0.190	1.903	99.68
W	0.527	1.365	71.52	Cu	0.095	1.905	99.80
Ta	0.512	1.458	76.39	Ba	0.082	1.907	99.89
Ce	0.492	1.539	80.62	Co	0.069	1.908	99.96
Ag	0.471	1.609	84.31	Sc	0.046	1.909	99.99
Sb	0.439	1.668	87.39	Zn	0.029	1.909	100
Be	0.435	1.724	90.31	Sr	0.000	1.909	100
Mo	0.413	1.773	92.87	V	0.000	1.909	100
La	0.369	1.811	94.86				

Note: AI and IC are explained by Hung et al. (2020) [2].

Following the three-sigma limit method, the geochemical samples are statistically performed in this study (Table 2). The mean value, variance, and coefficient of variation are all basic statistical metrics. Skewness and kurtosis techniques were used to test the element distribution models, and the majority of the element concentrations followed the geometric distribution criteria (Table 3). The Geostatistic 9.0 program evaluated the distribution models and statistical analysis [36].

The distribution rules of the indicator elements did not adhere to the normal standard distribution and were modified to geometric distribution, according to the characterizations of the statistical distribution of Sn and W elements in the secondary geochemical area (Table 3). The overall content of Sn and W components is greater than Clark's value in the crust ($Sn^*=2.5\text{ppm}$, $W^*=1.3\text{ppm}$ [37], where Sn and W concentration varies from uneven to extremely uneven. It is feasible to produce various geochemical anomalies on a local scale. As a result, the Sn and W elements might form small anomalies in the primary geochemical field. Nonetheless, this data may be utilized to discover geochemical dispersion haloes, which can be used to identify potential sites for Sn-W mineral exploration in the Dong Van region.

Table 2. Statistical characteristics of the indicator elements (ppm) in the Dong Van region

Parameters	Ag	As	Be	Pb	Bi	Sb	Ce	Sn	Ta	W	Ge	Li
Mean	1.27	49.39	5.67	27.9858	0.98	19.2444	87.55	14.6279	23.0603	19.7104	5.5618	46.403
Median	0.33	27.63	1.90	23.31	0.47	3.2	78.15	8.805	5.255	5.87	5	33.715
Mode	18.54	49.00	31.60	10.77	4.03	37.24	64.05	49.07	20.63	48.02	0	40.19
Standard deviation	13.10	75.83	29.49	21.7042	3.62	60.9511	40.018	45.4845	46.9017	61.1201	1.579	47.3386
Variance	171.60	5750.53	869.61	471.0731	13.09	3715.039	1601.45	2068.839	2199.772	3735.672	2.4934	2240.944
Coefficient of variation (%)	1029.03	153.55	520.29	77.55	371.94	316.72	45.71	310.94	203.39	310.09	28.39	102.02
Skewness	25.87	6.32	14.85	2.252	18.13	6.19	2.35	14.913	4.109	9.053	2.463	7.51
Kurtosis	717.33	52.41	270.95	9.444	384.99	47.879	7.91	273.92	22.217	106.11	4.073	83.746
Minimum	0.04	2.00	0.10	0.77	0.03	0.24	16.05	0.07	0.13	0.02	5	5.69
Maximum	370.70	945.65	636.31	209.29	85.61	743.58	337.75	986.44	415.76	967.95	10	703.89
Summary	1132.97	43954	5044.38	24907.39	865.90	17127.49	77916.67	13018.85	20523.7	17542.25	4950	41298.7

Table 3. Testing of the statistical distribution model of the Sn, W elements

Distribution model	Sn (ppm)							W (ppm)						
	Deviation	Actual deviation	Chi square (18.307)	Conforming to Chi square test	λ (1.358)	Conforming to Kolmogorov test	Synthesizer	Deviation	Actual deviation	Chi square (18.307)	Conforming to Chi square test	λ (1.358)	Conforming to Kolmogorov test	Synthesizer
Geometric	2.486	1	3.267	1-Yes	0.160	1-Yes	0.300	5.045	1	31.429	1-No	0.345	1-Yes	1.973
Gamma	24.441	2	61.592	2-No	1.562	2-No	4.515	22.369	2	51.685	2-No	1.470	2-No	3.906
Lognormal	61.402	3	164.788	3-No	3.412	3-No	11.514	32.496	3	88.052	3-No	1.889	3-No	6.201
Special discrete	104.029	5	459.352	4-No	7.294	5-No	30.463	58.635	4	147.230	4-No	3.282	4-No	10.459
Pareto	115.827	6	487.814	5-No	7.537	6-No	32.196	98.299	5	412.558	5-No	6.929	5-No	27.638
Exponential	94.306	4	606.050	6-No	6.356	4-No	37.7853	111.040	6	449.417	6-No	7.227	6-No	29.871
Binomial	287.065	10	926.397	7-No	20.737	10-No	65.874	281.168	10	1223.811	7-No	20.239	10-No	81.753
Normal	266.722	9	2150.286	8-No	14.912	7-No	128.438	260.992	9	2059.889	8-No	14.689	7-No	123.336
Triangular	234.503	7	4426.587	9-No	17.320	8-No	254.552	231.131	7	4598.079	9-No	17.081	8-No	263.743
Uniform	251.125	8	8564.185	10-No	18.822	9-No	481.669	244.535	8	8120.654	10-No	18.324	9-No	457.075

Note: The Kolmogorov-Smirnov test is introduced in Chakravarti et al. [32].

4.2. Cluster analysis

The correlation analysis findings may create a pair correlation matrix of the best indicator elements in the entire region's geochemical field. [Table 4](#) shows the elements of the pair correlation matrix between the good indicator items. The Be, Sn, W, and Bi elements create a tight association among the indicator element affiliations, particularly the link between Sn and W, establishing the element collaboration as an indication for exploring polymetallic ores.

Table 4. The correlation coefficient for indicator elements (ppm) in the sediment samples

	Ag	As	Be	Bi	Ce	Li	Pb	Sb	Sn	Ta	W
Ag	1										
As	0.032	1									
Be	0.062	0.445	1								
Bi	0.051	0.205	0.711	1							
Ce	0.026	0.262	0.082	0.142	1						
Li	0.044	0.425	0.569	0.542	0.386	1					
Pb	-0.009	0.310	0.173	0.057	0.331	0.333	1				
Sb	0.071	0.407	0.392	0.499	0.437	0.465	-0.027	1			
Sn	0.006	0.623	0.645	0.213	-0.027	0.377	0.325	0.106	1		
Ta	-0.021	-0.019	-0.045	-0.036	-0.000	-0.078	0.110	-0.073	0.041	1	
W	0.018	0.438	0.588	0.412	-0.048	0.400	0.264	0.176	0.666	0.138	1

Compared to Li-Pb elements, the correlation coefficients demonstrate a tighter association between Be, Sn, W, and Bi elements ([Table 4](#)), showing that Li-Pb elements dominate in rock-forming and ore-forming processes. The calculations demonstrate a close link between the elements Be, Sn, W, and Bi, indicating that they have paragenesis.

A dendrogram was created to determine the link between the researched items based on the findings of pair-correlation analysis among these good indicator elements in the secondary geochemical area. Pearson's correlation coefficients were used to measure the similarity of such indicator items. The findings allow for the creation of dendrograms for the whole sample in the Dong Van region ([Fig. 3](#)).

The dendrogram depicts the paragenetic link between element groupings. Polymetallic ore (including two sub-groups as, Be-Sn-W-Bi, and Li-Pb) and rock-forming elements are separated into two categories (comprise three sub-groups, i.e., As-Cd-Sc-Cr-Ce-La, Co-Ni-V, and Ga-Ge-Ba). Aside from the strong association between Be, Sn, W, and Bi elements, a reasonably continuous level of elements, local branching of Co-Ni-V elements can also be seen, indicating that Co, Ni, and V are not syngenetic components of the polymetallic ores in the region.

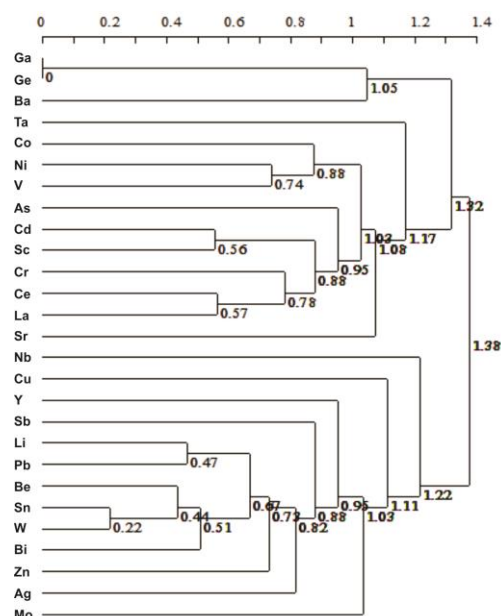


Fig. 3. Dendrogram diagram of the Dong Van region's geochemical elements (ppm). The numbers indicate the linkage distance cluster analysis using Ward's agglomerative clustering algorithm.

The use of a mixture of multivariate correlation and dendrogram analysis to determine the relevance of syngenetic element association for prospecting polymetallic ores in the study region. As a result, Be, Sn, W, and Bi are considered syngenetic. Despite the high amounts of the other elements, they are not indicators for finding polymetallic ores or mirroring the advent of another form of mineralization in this area.

4.3. Geochemical anomalous modeling

External circumstances can damage and modify ore bodies, mineralization zones, and the major geochemical field. Some elements and minerals are dissolved, washed, and floated away, while others collect and enhance the environment. The material elements of the secondary geochemical field are redistributed in the weathering environment. This field's distribution can occur on the terrain's surface and cover the original ore bodies. It can appear deeper in the terrain or a valley, and it can be considerably bigger than the ore bodies. The secondary localization field is critical in locating concealed mineral deposits in the prospecting region. Anomaly geochemical diagrams were utilized to simulate the spatial variation of the elements on the site's localization papers to detect polymetallic ore in the researched region.

Secondary geochemical anomalies of Sn and W elements were constructed to model the spatial field of excellent indicator elements as an indication for prospecting and locating new polymetallic ores in the Dong Van region. Creating these elements' anomalous geochemical diagrams seeks to reveal the distribution, concentration, and accumulation of geochemical anomalies in specific ore bodies in the specified location (Figs. 4, 5). It allows for the explanation and selection of anomalies connected with mineralization and the elimination of anomalies that do not pertain to a single ore on this basis.

The isoelectric contour lines with varying content degrees are mapped following the geochemical background and local anomalous values to calculate the indicator elements' geochemical anomaly and anomalous fields. The anomalous thresholds of the first-order (mean \pm 1 STD), second-order (mean \pm 2 STD), and third-order (mean \pm 3 STD) values are selected using the statistical processing findings to estimate the geochemical background value based on the local average value (Table 5, Figs. 4, 5), in which, the mean and STD values are calculated following the geometric distribution. Geochemical anomalies associated with metallization can be selected, and geochemical anomalies not related to polymetallic mineralization can be rejected based on the establishment of anomalous geochemical diagrams of the indicator elements and combined with documents of the prospecting works for checking the geochemical anomalies.

Table 5. Anomaly values of Sn, W are based on the anomaly thresholds which determining by calculated, theoretical, and probability standard deviation in the Dong Van region

Element (ppm)	Method	Clarke value	Back-ground	First-order anomaly	Second-order anomaly	Third-order anomaly	Anomaly
Sn	Calculated standard deviation (CSD)	2.5	19	65	110	156	156
	Theoretical standard deviation (TSD)	2.5	19	19	20	20	20
	Probability standard deviation (PSD)	2.5	19	38	57	76	76
	Probability distribution (PPD)	2.5	19	36	49	868	868
W	Calculated standard deviation (CSD)	1.3	19	81	142	203	203
	Theoretical standard deviation (TSD)	1.3	19	20	20	20	20
	Probability standard deviation (PSD)	1.3	19	38	56	75	75
	Probability distribution (PPD)	1.3	19	37	75	856	856

Note: Clark values of the indicator elements ($Sn^*=2.5ppm$, $W^*=1.3ppm$) in the crustal earth are from Fortescue [33].

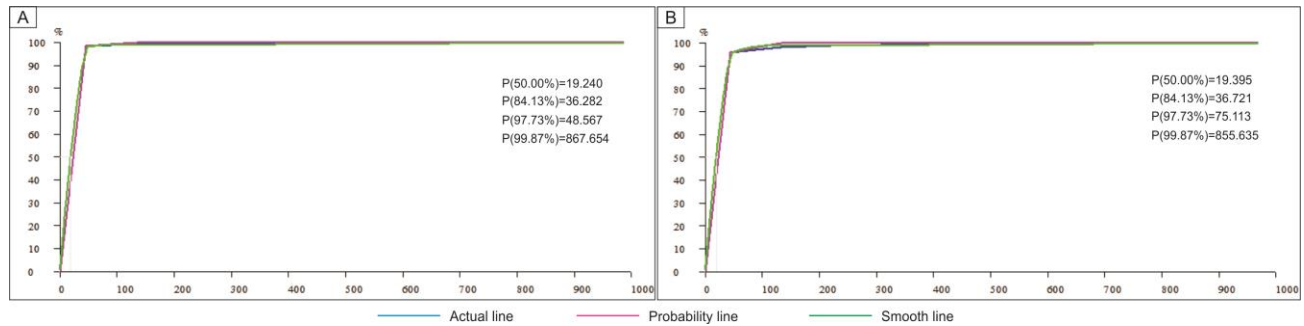


Fig. 4. Occurrence graphs of the Sn (A) and W (B) elements following geometric distribution in the Dong Van region, showing the probability of three anomaly thresholds and background.

The concentration of tin-forming ore bodies in the mineralized zone is reflected by geochemical anomalies of Sn and W elements. The geochemical anomalies of the indicator elements are distributed in three separate locations, as shown by the distribution area of the geochemical anomalies (Fig. 5). The geochemical anomalies are often isotropic or elliptical, extending northwest-southeast in accordance with the mineralization zone's established orientation. Most of the geochemical anomalies correspond to the Song Hien Formation's distribution region. The geochemical anomalies, particularly the tin and tungsten geochemical anomalies adjacent to the mineralized zone, are relatively vast and have a complex shape,

indicating the presence of concealed ore bodies associated with granitoid massive. The geochemical anomalies unrelated to mineralization are often limited secondary accumulations centered on low terrain slopes and rely on the existing terrain's shape.

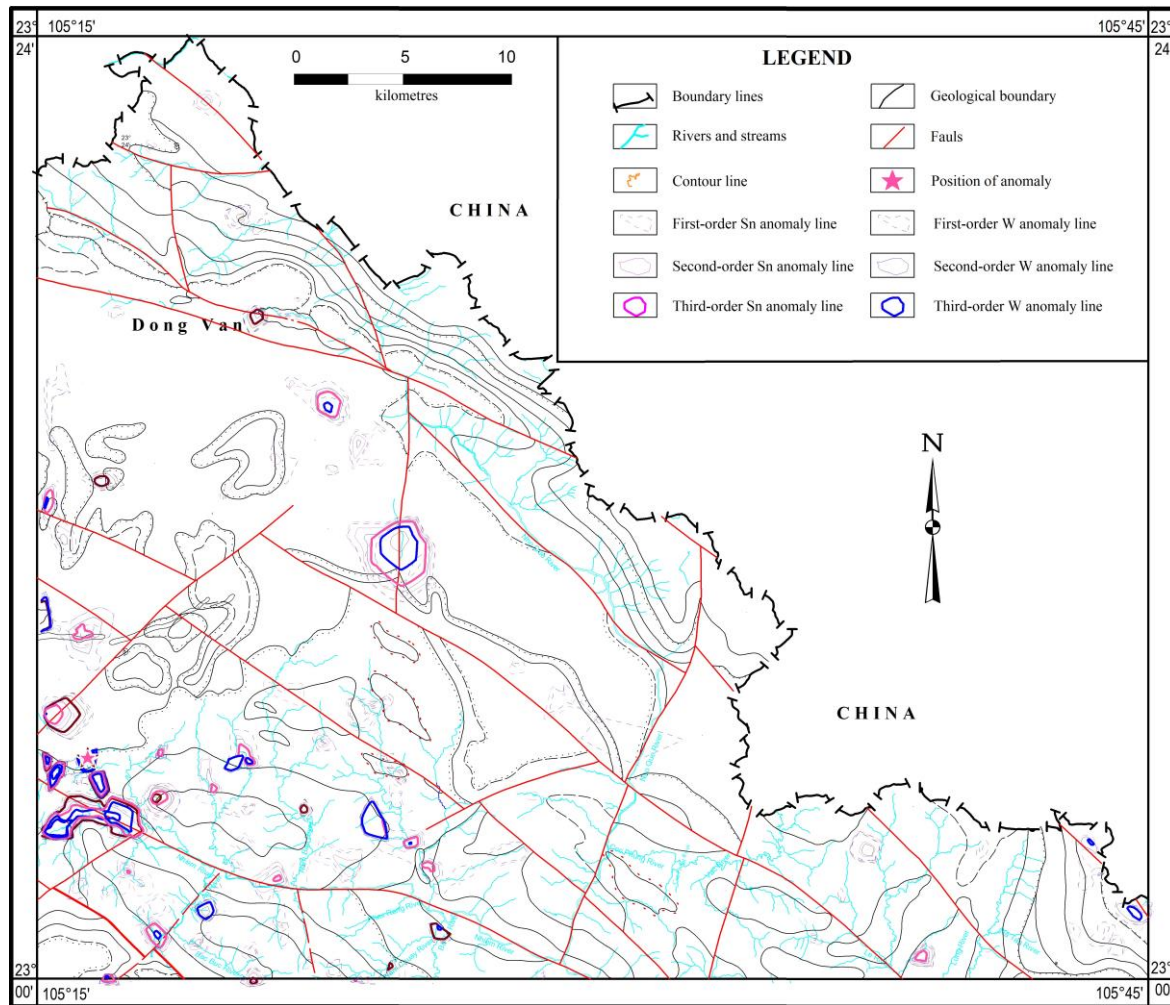


Fig. 5. General map of the Dong Van region, showing Sn, W anomaly indicating prospective areas

5. Conclusions

In conclusion, polymetallic mineralizations from the Dong Van area, northeastern Vietnam were studied using statistical and multivariate analytic approaches based on 890 geochemical samples. The following are the findings that can be derived from this research.

The findings of frequency analysis demonstrate that the Pb, As, Bi, Li, Sn, W, Ta, Ce, Ag, Sb, and Be elements have a strong relationship with polymetallic ore, implying that these elements can be used as indicators when prospecting for polymetallic mineralization. Furthermore, extensive anomalies in Sn and W elements exist in the Dong Van region, providing important information for polymetallic prospecting in the area. In the examined region, correlation matrix and dendrogram studies may also be used to divide the

elements into polymetallic ore-forming (including Be-Sn-W-Bi, and Li-Pb sub-groups) and rock-forming (i.e., As-Cd-Sc-Cr-Ce-La, Co-Ni-V, and Ga-Ge-Ba sub-groups) groups.

The threshold value (mean \pm 3 STD) is then utilized to determine polymetallic mineralization in the region by identifying anomalous locations and background levels of the indicator elements. In general, the promising locations are well-placed for recognized polymetallic mineral deposits.

The local factors of Sn and W elements are comparable, according to the geochemical modeling study and distribution of localized anomalous regions of the indicator elements. This suggests a link between polymetallic mineralization and the northwest-southeast fault system and concealed granitoid blocks in the area.

Finally, due to the relationship with the localization anomalies created during the statistical process, the statistical analysis of the bottom sediments reveals a potential for exploring polymetallic mineralization in the region. Furthermore, the findings show that the occurrence of polymetallic mineralization might have a positive geographical association. This is supported by statistical analysis and the definition of potential regions based on the geochemical data analysis threshold value of indicator elements.

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