

MINERAL AND GEOCHEMICAL ZONING OF THE MILIN KAMAK DEPOSIT, WESTERN SREDNOGORIE (BULGARIA): INSIGHTS FROM STATISTICAL ANALYSIS

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ABSTRACT. Statistical processing of geochemical data obtained during the detailed exploration of the *Milin Kamak* deposit was performed using univariate statistical analysis and Pearson correlation matrices. The results confirm a clear geochemical zonality consistent with previously published mineralogical and geochemical studies. Descriptive statistics reveal systematic differences in element distributions across the ore zones: gold attains its highest mean concentrations in Ore Zone 1, lead and zinc peak in the western sector of Zone 1, while arsenic shows elevated values in Zones 3 and 6. Correlation analysis demonstrates that gold exhibits a broad multi-element positive correlation with Ag, As, Bi, Cd, Cu, Pb, S, Sb, and Zn in the western sector of Ore Zone 1, consistent with the sulphosalt-bearing paragenesis, while in the eastern sector the correlation cluster is reduced and gold associates primarily with As and Mn. The Au–As correlation is strongest in the western sector ($r = 0.743$) and remains statistically significant across all ore zones ($r = 0.351$ – 0.569), identifying arsenic as the sole reliable deposit-wide pathfinder for gold. Calcium and magnesium show a consistent negative correlation with gold in all zones, marking intervals lacking ore mineralization.

Key words: zonal distribution, epithermal deposit, statistics, 3D modelling.

МИНЕРАЛНА И ГЕОХИМИЧНА ЗОНАЛНОСТ НА НАХОДИЩЕ „МИЛИН КАМЪК“, ЗАПАДНО СРЕДНОГОРИЕ (БЪЛГАРИЯ): ИНТЕРПРЕТАЦИЯ НА БАЗА СТАТИСТИЧЕСКИ АНАЛИЗ

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РЕЗЮМЕ. Извършена е статистическа обработка на геохимични данни от детайлното проучване на находище „Милин камък“ чрез прилагане на едномерен статистически анализ и корелационни матрици на Пирсън. Резултатите потвърждават ясно изразена геохимична зоналност, съответстваща на публикуваните минералогични и геохимични изследвания. Дескриптивната статистика показва систематични различия в разпределението на елементите между рудните зони: златото е с най-високи средни съдържания в рудна зона 1, оловото и цинкът достигат максимум в западния участък на зона 1, а арсенът е повишен в зони 3 и 6. Корелационният анализ показва, че в западния участък на зона 1 златото има широка многоелементна положителна корелация с Ag, As, Bi, Cd, Cu, Pb, S, Sb и Zn, съответстваща на сулфосолната парагенеза, докато в източния участък корелационният клъстер е редуциран и златото асоциира предимно с As и Mn. Корелацията Au–As е най-силна в западния участък ($r = 0.743$) и остава статистически значима във всички рудни зони ($r = 0.351$ – 0.569), което определя арсена като единствен надежден индикатор за злато в находището. Калцият и магнезият показват последователна отрицателна корелация със златото във всички зони, маркирайки интервали, в които липсва рудна минерализация.

Ключови думи: зонално разпределение, епитермално находище, статистика, 3Д моделиране.

Introduction

The *Milin Kamak* deposit is situated in the Western Srednogorie zone, within the municipality of Breznik, southwestern Bulgaria, and belongs to the Late Cretaceous Apuseni–Banat–Timok–Srednogorie (ABTS) magmatic and metallogenic belt (Popov et al., 2002). Intensive exploration activities carried out between 2004 and 2019 classified the deposit as an intermediate sulphidation epithermal gold–silver system with associated Pb, Zn, and Cu mineralisation (Sabeva et al., 2012). Ore formation proceeded through three successive hydrothermal stages — quartz–pyrite, quartz–polymetallic, and carbonate–gold — as established by Sabeva and Mladenova (2012) and Sabeva et al. (2017), who also documented the hydrothermal alteration zonality, fluid inclusion data, and sulphur isotope systematics of the deposit. The mineral composition of Ore Zone 1 was subsequently detailed by Nikolova et al. (2019), who reported previously undescribed phases including seligmanite, gratonite, jordanite, and robinsonite, and confirmed that native gold is high-fineness rather than electrum. Gold was deposited through both the quartz–pyrite stage and the quartz–sulphosalt stage. Recent investigations have further expanded the metallogenic interpretation of the deposit, indicating the presence of potential silver mineralisation in the southern periphery of the deposit (Iovchev, Strahilov, 2026).

The spatial distribution of geochemical associations was previously examined by Marinov et al. (2019) using multivariate factor analysis applied to a dataset of 36,615 samples, resulting in the identification of six factor groups. Of these, three — [Cd, Zn, Pb], ([Cu, Sb] Bi) Ag, and ([As] Au) Mn — show a clear spatial relationship to the ore bodies, including a pronounced west-to-east zonality along Ore Zone 1. Nikolova (2022) subsequently provided the mineralogical interpretation of these factor associations, linking each to a specific ore-forming mineral assemblage.

A systematic quantitative characterisation of geochemical zonality through univariate statistical analysis and inter-element correlation matrices has not been published. The behavior of individual elements across the ore zones — and in particular the spatially varying correlation structure of gold with potential pathfinder elements — has not been described. Such an analysis is essential for establishing reliable geochemical indicators for targeted exploration and for integrating the statistical evidence with the established mineralogical framework.

The present study addresses this gap by applying one-dimensional statistical analysis and Pearson correlation matrices to the full geochemical dataset obtained during the detailed exploration program of 2016–2019. The specific objectives are: (1) to characterise the distribution of key ore-forming elements across the individual ore zones through

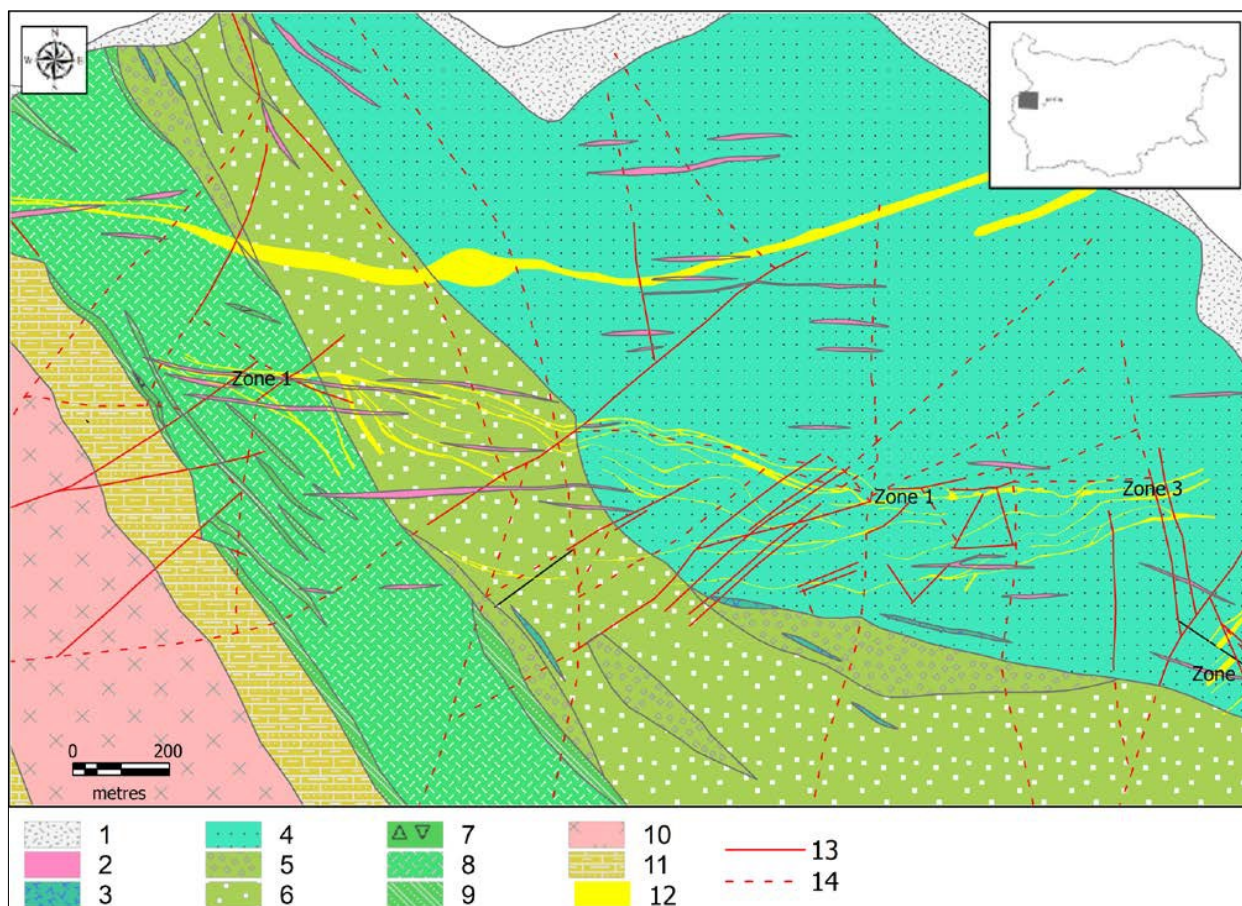


Fig. 1. Geological map of the Milin Kamak deposit and Ore Zones (after Nikolova, 2019). 1. Alluvial sediments; 2. Basaltic andesite dyke; 3. Basalt and basaltic andesite lavas; 4. Agglomerate tuffs; 5. Bomb – block tuffs; 6. Lapilli – psephytic tuffs; 7. Trachybasalt lavas; 8. Lapilli tuffs; 9. Beds of psephytic and pellitic tuffs; 10. Trachyandesites (plagioclase); 11. Sediment alternation; 12. Ore zone; 13. Certain fault; 14. Supposed fault.

descriptive statistics; (2) to assess the correlation structure of gold with associated elements within individual ore zones and between sectors of Ore Zone 1; and (3) to synthesise the statistical, mineralogical, and factor-analytical evidence into a unified description of the geochemical and mineralogical zonality of the *Milin Kamak* deposit.

Geological Settings

Regional Geological Framework

The *Milin Kamak* deposit is located approximately 3 km southeast of the town of Breznik (Fig. 1). It is spatially and genetically associated with the Breznik paleovolcano, a Late Cretaceous central-type volcanic structure. The host rocks comprise trachybasalt and shoshonitic lavas, agglomerate, lapilli, and bomb–block tuffs, and basaltic andesite dykes (Dabovski et al., 2009). The volcanic succession reaches up to 1,400 m in thickness in the deposit area.

The principal ore-controlling structures are east–west trending faults dipping steeply to the south (Fig. 1). These are cross-cut by ENE–WSW and NNW–SSE faults of secondary importance (Strahilov et al., 2022, Strahilov, Marinov, 2025). Recent geomechanical analysis by Strahilov (2024) provides additional insight into the relationship between the deposit's structural framework and rock mass behavior.

The deposit is situated along the southern limb of the Krasava syncline, which has influenced the southward tilting of the ore zones (Marinov et al., 2019).

Hydrothermal alteration is pervasive and zonally developed, comprising propylitic, sericitic, argillic, and advanced argillic types (Sabeva et al., 2017). Potassic alteration in the deeper eastern portion of the deposit has been interpreted as indicating proximity to a concealed porphyry-type source (Novakova et al., 2024).

Eight ore zones have been delineated localised in veins hosted by lapilli tuffs and basalt dykes. The zones are east–west oriented and steeply south-dipping, with the exception of Ore Zone 7, which trends northeast–southwest. Ore Zone 1 is the largest, with a strike length exceeding 1 km. It is subdivided into eastern and western sectors on structural and compositional grounds. The mineral paragenesis comprises three successive stages: quartz–pyrite, quartz–polymetallic, and carbonate–gold (Sabeva et al., 2012).

Materials and Methods

Dataset

The geochemical dataset was obtained during the detailed exploration program conducted between 2016 and 2019 by Trace Resources Ltd. The program comprised over 40,000 sampled intervals.

Core samples were split longitudinally; one half was retained for analysis and the other archived. Samples were dried at 105°C, crushed to 2 mm, split using a Jones riffle splitter, and pulverised to 200 mesh. Analysis was carried out at the ALS laboratory, by inductively coupled plasma atomic emission spectrometry (ME-ICP61) following four-acid digestion, covering 33 elements. Gold was determined by fire assay with atomic absorption finish (Au-AA26, up to 100 ppm) and by fire assay with gravimetric finish (Au-GRA22, above 100 ppm).

Twelve elements were excluded from statistical processing as they do not participate in ore-forming processes and occur predominantly below detection limits (Al, Ga, K, La, Na, Ni, P, Sc, Sr, Th, Ti, U). Values below the detection limit were substituted by one-half of the respective lower detection limit (Marinov, 2019). The final dataset comprises 22 elements: Ag, As, Au, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Ti, V, W, and Zn.

Statistical Methods

The statistical analysis followed the sequential methodology developed by Popov (2016), previously applied to the *Milin Kamak* deposit by Marinov et al. (2019). The full workflow comprises: (1) preliminary data preparation; (2) univariate statistical analysis; (3) correlation and cluster analysis; and (4) factor analysis with 3D modelling. Stages 3 and 4 have been published in Marinov et al. (2019) and Nikolova (2022). The present study focuses on stages 1 and 2, drawing on the published factor-analytical results for comparative interpretation only.

Univariate statistical analysis was applied to characterise element distributions within each ore zone. The following parameters were computed: arithmetic mean, standard deviation, coefficient of variation, skewness, and kurtosis. Analysis was performed separately for the eastern and western sectors of Ore Zone 1 and for Ore Zones 2, 3, 5, and 6.

Correlation analysis was performed using the Pearson product-moment correlation coefficient (r). Correlation matrices were constructed for each spatial subdivision, with gold positioned as the first variable. Correlations with $|r| \geq 0.3$ were considered geochemically significant, consistent with the sample sizes involved.

Results

Distribution of Elements across Ore Zones

Descriptive statistical analysis was performed for six spatial subdivisions: the eastern and western sectors of Ore Zone 1, and Ore Zones 2, 3, 5, and 6. The frequency distributions of all ore-forming elements exhibit strongly positive skewness and right-tailed histograms. This pattern is characteristic of hydrothermal mineralisation superimposed on an unmineralised volcanic host and is consistent with observations from epithermal systems of the ABTS belt (Popov, 2002).

Gold attains its highest mean concentrations in Ore Zone 1, with the eastern sector recording values approximately twice those of the western sector. Mean Au contents decrease markedly toward Zones 2 and 5, reaching their lowest values in Zones 3 and 6. Silver shows an inverse relationship with gold: zones with higher mean Au correspond to lower mean Ag values, indicating that the Au/Ag ratio varies systematically across the deposit.

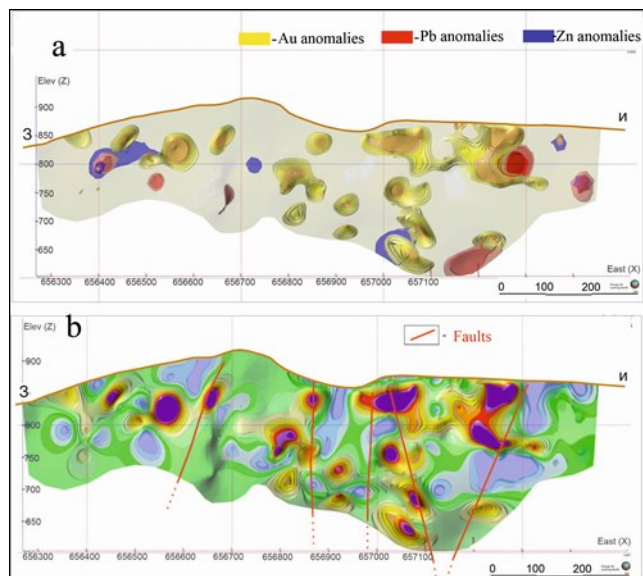


Fig. 2 – a - vertical projection of Zone 1 with zonal distribution of Au, Pb, and Zn; b – Longitudinal vertical projection of Zone 1 with Au geochemical anomalies (Au concentrations increase from cool to warm colors) relative to oblique steep to gentle NNE-SSW and NE-SW faults.

Lead and zinc display a distribution pattern distinct from that of gold. Both elements attain their highest mean concentrations in the western sector of Ore Zone 1 (Fig. 2), where mean Pb values exceed those of the eastern sector by a factor of approximately four. Zones 2 and 5 show intermediate Pb and Zn contents, while Zones 3 and 6 record the lowest values. The strong Pb–Zn co-variation across all zones reflects their common host in the galena–sphalerite assemblage.

Arsenic shows a contrasting distribution relative to Pb and Zn. Mean As concentrations are the highest in Zones 3 and 6, where Pb and Zn are the lowest. This inverse spatial relationship between As and the Pb–Zn pair is one of the clearest statistical expressions of geochemical zonation in the deposit. Copper and antimony follow a distribution broadly analogous to that of gold, with elevated mean values in the central and eastern portions of the deposit.

Calcium and magnesium are decoupled from the sulphide ore-forming elements. Their distribution is inversely related to the majority of ore metals across all zones, as discussed further in the correlation analysis below.

Pearson Correlation Analysis

Pearson correlation matrices were computed for gold against all remaining 21 elements within each spatial subdivision. The Au correlations are summarised in Table 1.

Ore Zone 1 — Western Sector. Gold exhibits the strongest Au–As correlation recorded in the deposit ($r = 0.743$). Beyond arsenic, gold participates in a broad multi-element positive correlation cluster: S ($r = 0.429$), Zn ($r = 0.394$), Cd ($r = 0.391$), Cu ($r = 0.371$), Ag ($r = 0.370$), Pb ($r = 0.365$), Sb ($r = 0.327$), Bi ($r = 0.303$), and Fe ($r = 0.298$). The simultaneous positive correlation of Au with both the Pb–Zn–Cd suite and the Cu–Sb–Bi suite indicates that gold in this sector is spatially associated with the full range of sulphide and sulphosalt assemblages. The Au–Mn correlation is modest ($r = 0.184$). Gold shows negative correlations with Mg ($r = -0.409$) and Ca ($r = -0.348$), reflecting

the inverse relationship between the sulphide ore assemblage and the late rhodochrosite veining.

Ore Zone 1 — Eastern Sector. The Au–As correlation remains strong ($r = 0.513$) but is weaker than in the western sector. The multi-element correlation cluster is substantially reduced. Sb ($r = 0.325$), Cu ($r = 0.291$), S ($r = 0.264$), and Fe ($r = 0.222$) retain moderate positive correlations with Au, while Ag ($r = 0.220$), Pb ($r = 0.171$), Zn ($r = 0.171$), Cd ($r = 0.184$), and Bi ($r = 0.211$) are markedly weaker than in the western sector. The Au–Mn correlation strengthens in the eastern sector ($r = 0.301$), reflecting the greater spatial association of gold-bearing intervals with Mn-carbonate veining. Negative correlations with Mg ($r = -0.337$) and Ca ($r = -0.301$) are preserved.

Table 1. Gold correlation with other chemical elements for ore zones 1, 2, 3, 5, and 6

	Zone 1 west	Zone 1 east	Zone 2	Zone 3	Zone 6	Zone 5
Ag	0.37	0.22	0.161	0.314	0.354	0.332
As	0.743	0.513	0.351	0.536	0.497	0.569
Bi	0.303	0.211	0.057	0.050	0.050	0.29
Cd	0.391	0.184	0.048	0.391	0.242	0.197
Cu	0.371	0.291	0.060	0.152	0.429	0.217
Fe	0.298	0.222	0.097	0.175	0.050	0.282
Mn	0.184	0.301	0.147	0.367	0.432	0.050
Pb	0.365	0.171	0.112	0.151	0.202	0.231
S	0.429	0.264	0.191	0.341	0.219	0.34
Sb	0.327	0.325	0.125	0.262	0.468	0.22
Zn	0.394	0.171	0.056	0.365	0.236	0.193
Ca	-0.348	-0.301	-0.199	-0.196	0.050	-0.362
Mg	-0.409	-0.337	-0.193	-0.232	-0.106	-0.365

The contrasting correlation structures of the two sectors indicate that in the western sector gold is spatially linked to the full sulphide paragenesis, while in the eastern sector it associates more specifically with As-bearing phases and Mn-carbonates. This is consistent with the mineralogical observations of Nikolova (2022), who documented the dominance of pyrite–arsenopyrite in the eastern drill holes and the maximum development of sulphosalt and galena–sphalerite minerals in the western and central portions of Ore Zone 1.

Ore Zones 2, 3, 5, and 6. Arsenic maintains a consistently positive correlation with gold across all zones: $r = 0.351$ (Zone 2), 0.536 (Zone 3), 0.497 (Zone 6), and 0.569 (Zone 5). Silver shows moderate Au correlations in Zones 3 ($r = 0.314$), 5 ($r = 0.332$), and 6 ($r = 0.354$), and a weak correlation in Zone 2 ($r = 0.161$). Manganese exhibits moderate positive Au correlations in Zones 3 ($r = 0.367$) and 6 ($r = 0.432$), but is uncorrelated in Zone 5 and weakly correlated in Zone 2 ($r = 0.147$). Copper shows a notably strong Au correlation in Zone 6 ($r = 0.429$). The correlations of Au with Pb, Zn, Cd, Bi, and Fe are generally weak across these zones, with several elements recording near-zero coefficients.

Calcium shows negative Au correlations in Zones 1, 2, 3, and 5, ranging from $r = -0.199$ to $r = -0.362$, while in Zone 6 the correlation is absent. Magnesium maintains a negative Au correlation in all zones without exception, ranging from

$r = -0.106$ (Zone 6) to $r = -0.409$ (Zone 1 west). Magnesium is thus the most consistently inverse geochemical indicator relative to gold in the deposit.

Discussion

Geochemical, Mineralogical, and Factor-Analytical Evidence for Zonality

The statistical results presented above provide quantitative confirmation of the spatial geochemical zonality previously inferred from mineralogical observations (Nikolova et al., 2019; Nikolova, 2022) and three-dimensional factor modelling (Marinov et al., 2019). Three independent lines of evidence — descriptive statistics, correlation analysis, and factor analysis — converge on a coherent and internally consistent picture of element distribution within the deposit, illustrated schematically in Fig. 3.

The western sector of Ore Zone 1 is characterised by elevated mean Pb and Zn concentrations and a broad multi-element Au correlation cluster. This pattern corresponds directly to the spatial domain of Factor 1 [Cd, Zn, Pb] identified by Marinov et al. (2019) and is mineralogically explained by the predominance of the quartz–galena–sphalerite assemblage (Nikolova, 2022). The strong Cd–Zn correlation reported for this association reflects the well-known isomorphic substitution of Cd for Zn in sphalerite under stable physicochemical conditions (Cook et al., 2009).

The central sector of Ore Zone 1 and its continuation into Zone 2 at depth correspond to Factor 4 ([Cu, Sb] Bi) Ag of Marinov et al. (2019). The present correlation analysis confirms this through moderately strong Au–Cu, Au–Sb, Au–Bi, and Au–Ag correlations in the western sector of Zone 1, where the sulphosalt assemblage reaches its maximum development. This association is mineralogically carried by the tennantite–tetrahedrite and seligmanite–bournonite series (Nikolova, 2022). The positive Cu–Ag correlations point to isomorphic substitution in tetrahedrite, while the Ag–Pb–Sb–Bi correlations indicate the presence of Sb- and Bi-bearing galena microinclusions.

The eastern sector of Ore Zone 1, and to a lesser extent Zones 3, 5, and 6, are dominated by the Au–As correlation, consistent with Factor 6 ([As] Au Mn) of Marinov et al. (2019). This association represents the main ore body and coincides with the highest gold concentrations in the deposit. The Au–As relationship reflects two mechanisms: the occurrence of submicroscopic invisible gold in arsenian pyrite through lattice substitution of the type $\text{Au}^{3+} + \text{As}^- \Rightarrow 2\text{Fe}^{2+}$ (Arehart et al., 1993), and the association of visible native gold with arsenopyrite and marcasite in the quartz–polymetallic and carbonate–gold stages (Nikolova et al., 2019). The positive Au–Mn correlation in this sector reflects the spatial co-occurrence of gold-bearing intervals with rhodochrosite veining, which marks the final carbonate–gold stage. The consistent negative correlation of Au with Ca and Mg across all zones confirms that the bulk carbonate matrix is not a productive host for gold and functions as a negative geochemical indicator.

The overall zonality pattern — Pb–Zn mineralisation in the western sector, a Cu–Sb–Bi–Ag sulphosalt-dominated central zone, and an As–Au–Mn association in the eastern sector and peripheral zones — is consistent with a lateral temperature gradient within the hydrothermal system. Low-temperature distal mineralisation represented by the galena–sphalerite

assemblage occupies the western periphery, while higher-temperature assemblages including sulphosalts and arsenopyrite characterise the central and eastern sectors. This interpretation is supported by fluid inclusion homogenisation temperatures of 238–345 °C reported by Sabeva et al. (2017) for Ore Zone 1, and by the occurrence of enargite exclusively in

the eastern portions and deeper drill holes (Nikolova et al., 2019). The identification of potassic alteration in the deeper eastern sector (Novakova et al., 2024) further supports the interpretation of a telescoped hydrothermal system with a concealed porphyry-type center at depth, in accordance with the genetic model of Moritz et al., 2007.

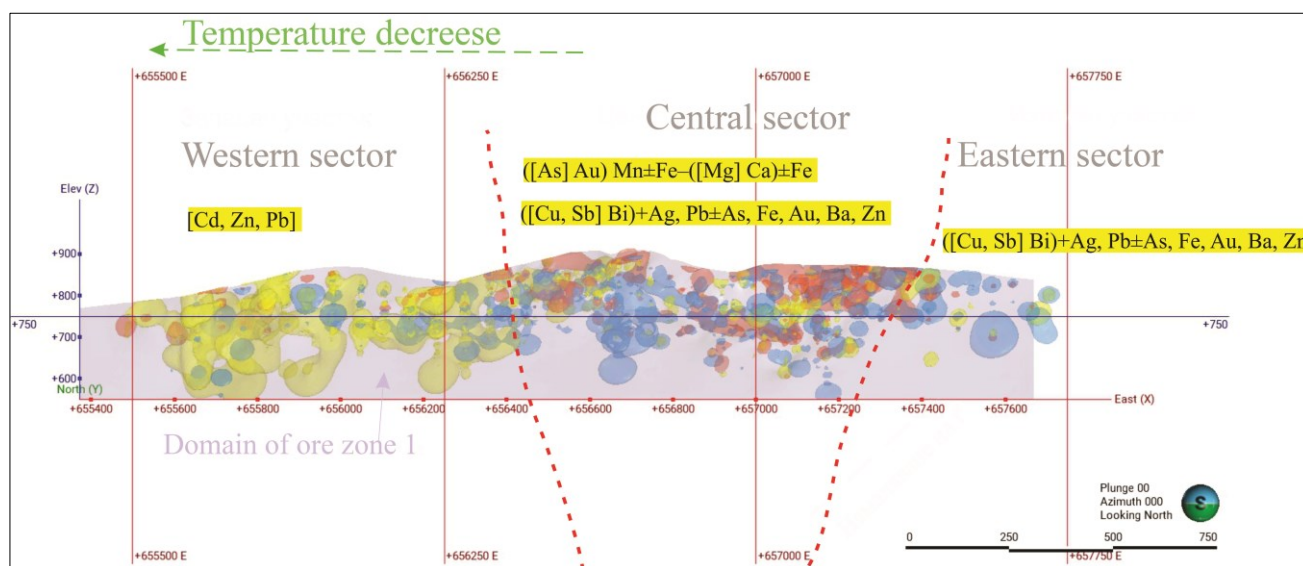


Fig. 3 A generalised section model by individual factors and their location in the Milin Kamak area

Arsenic as a Geochemical Pathfinder for Gold

Arsenic is the only element that maintains a statistically significant positive correlation with gold in every ore zone examined, with r values ranging from 0.351 in Zone 2 to 0.743 in the western sector of Zone 1. All other elements show spatially variable and zone-dependent correlations with Au, rendering them unreliable as universal indicators across the full extent of the deposit.

The reliability of As as an Au pathfinder in epithermal systems is well established. In pyrite, arsenic facilitates gold uptake through lattice substitution and surface adsorption on As-rich growth zones. In arsenopyrite, gold occurs as structurally bound invisible gold or as nanoscale native gold inclusions (Arehart et al., 1993). Both hosts are present at Milin Kamak (Nikolova et al., 2019). The deposit-wide character of the As–Au relationship is further confirmed by the spatial distribution of Factor 6 ([As] Au Mn) across the full length of Zone 1 and into Zone 2 (Marinov et al., 2019).

The attenuation of the Au–As correlation in Zone 2 ($r = 0.351$) relative to the remaining zones likely reflects a lower abundance of As-bearing mineral phases or greater dilution by barren intervals rather than a fundamental discontinuity in the hydrothermal system.

From an exploration perspective, As anomalies in intervals with subeconomic Au contents — particularly in the distal parts of the ore zones and at depth — should be regarded as significant exploration targets. Conversely, the consistent negative Au–Mg correlation ($r = -0.106$ to -0.409) provides a complementary negative indicator. The combined use of As as a positive and Mg as a negative geochemical indicator offers a practical tool for prioritising drill hole intervals.

Conclusions

Univariate statistical analysis and Pearson correlation matrices applied to a dataset of over 40,000 drill hole intervals from the Milin Kamak deposit yield the following principal conclusions.

Descriptive statistics reveal a well-defined geochemical zonality across the ore zones. Gold attains its highest mean concentrations in Ore Zone 1 and decreases systematically toward the peripheral zones. Lead and zinc peak in the western sector of Zone 1 and decrease eastward, while arsenic shows an independent distribution with elevated values in Zones 3 and 6. The inverse Au–Ag relationship across all zones indicates that the Au/Ag ratio is a meaningful indicator of mineralisation style and spatial position.

The correlation structure of gold differs fundamentally between the two sectors of Ore Zone 1. In the western sector, gold participates in a broad multi-element positive correlation cluster encompassing Ag, As, Bi, Cd, Cu, Pb, S, Sb, and Zn, consistent with the sulphosalt-bearing quartz–polymetallic assemblage. In the eastern sector, the correlation cluster is reduced and gold associates primarily with As and Mn, reflecting the dominance of the pyrite–arsenopyrite paragenesis and Mn–carbonate veining.

Arsenic is the only element that maintains a statistically significant positive correlation with gold across all ore zones ($r = 0.351$ – 0.743). It is identified as the sole reliable deposit-wide geochemical pathfinder for gold. The consistent negative Au–Mg correlation across all zones ($r = -0.106$ to -0.409) indicates that Mg-rich intervals are associated with propylitic wall-rock alteration rather than productive sulphide-bearing mineralisation. Magnesium therefore serves as a reliable negative geochemical indicator, effectively marking Au-barren intervals.

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