

Stream sediments geochemistry in the Valongo anticline, northern Portugal: arsenic as a proxy to outline new exploration targets

Geoquímica de sedimentos de corrente no Anticlinal de Valongo, norte de Portugal: arsénio como um indicador para delinear novos alvos de exploração

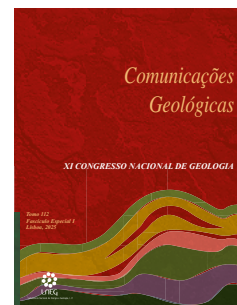
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DOI: <https://doi.org/10.34637/k72t-r759>

Recebido em 01/10/2023 / Aceite em 08/01/2024

Publicado online em abril de 2025

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Artigo original
Original article

Abstract: The Valongo anticline is known for the occurrence of several Sb-Au and As-Au mineral deposits, many of which have been exploited since Roman times. The Sb-Au and As-Au deposits occur in brecciated quartz veins, predominantly trending NE-SW, NNW-SSE, and ENE-WSW, cutting Cambrian to Carboniferous formations. An 801-stream sediment campaign was conducted in this area. Factorial kriging was applied as an interpolation method as it enables the estimation and mapping of the individual spatial components of the variogram. Arsenic (As) was used as a proxy to outline new exploration targets. The results allow the identification of NW-SE and NE-SW alignments as preferential areas for elevated As contents. Future studies will incorporate structural information and the distribution of old mine dumps to achieve higher accuracy in target areas for mining prospecting.

Keywords: Exploration, stream sediments, geochemical background, exploration targets, Au deposits.

Resumo: O anticlinal de Valongo é conhecido pela ocorrência de vários depósitos de Sb-Au e As-Au, muitos deles explorados desde os tempos romanos. Os depósitos de Sb-Au e As-Au ocorrem nos filões de quartzo com estrutura brechóide com direção predominante NE-SW, NNW-SSE e ENE-WSW cortando formações do Câmbrio ao Carbónico. Uma campanha de 801 sedimentos de corrente foi obtida nesta área. A krigagem factorial foi aplicada como um método de interpolação, pois permite a estimativa e mapeamento dos diferentes componentes espaciais do variograma. O arsénio (As) foi usado como proxy para o delineamento de possíveis novos alvos de exploração. Os resultados permitem a identificação de alinhamentos NW-SE e NE-SW, como preferenciais para teores elevados de As. Estudos futuros irão usar informação estrutural e a distribuição das antigas escombrelas para obter uma maior precisão nas áreas para prospeção mineira.

Palavras-chave: Exploração mineral, fundo geoquímico, alvo de exploração, sedimentos de corrente, depósitos de Au.

1. Introduction

The Valongo anticline is known for the occurrence of many mineral deposits and old mines, with a predominance of Sb-Au deposits, some exploited since Roman times, but especially in the late 19th century. The definition of advanced-stage exploration targets has long resorted to the analysis of the spatial distribution patterns of trace elements (or indicator minerals) in stream sediments (*e.g.* Wang *et al.*, 2022). It is key that the data analysis approach may allow the distinction between patterns related to local (delimited) sources, diffuse (background) sources or random distribution.

This study aims: 1) to identify and model the geochemical anomalies of arsenic considering its association to the mineral paragenesis of Sb-Au deposits; 2) to recognize possible spatial anisotropies and high significance clusters of As in the Valongo anticlinal; 3) to find the natural (*e.g.* geological formations, mineral deposits) and anthropogenic sources (*e.g.* mine tailings, foundries' slag).

2. Geological setting

Located 18 km from Oporto, the Valongo anticline includes Cambrian to Carboniferous formations (Figura 1A, B). It is asymmetric and trends NW-SE, with a synclinal to the west. The Cambrian phyllites with metagraywackes are overlapped, in angular unconformity, by Tremadocian-Floian metaconglomerates followed by a sequence of quartzites, phyllites, metasandstone, and graphitic phyllites with metavolcanic intercalations. The Lower Ordovician sequence is followed by the Dapingian-Darriwilian black shales, and by Hirnantian quartzites, with pelite and metagraywacke intercalations (Medeiros *et al.*, 1980). The Silurian is represented by black shales and quartzites in both anticline flanks. On the western flank of the anticline, Devonian is represented by clay shales, thin sandstone beds and quartzites (Medeiros *et al.*, 1980). The Carboniferous is represented by sedimentary breccia, black clay shales and alternating conglomerates, sandstone, and arkoses, with coal intercalations and also occurs on the western flank of the anticlinal. Variscan granites surround the Valongo anticline (Carvalho *et al.*, 2012) (Figura 1B).

The Sb-Au and As-Au deposits occur in brecciated quartz veins, with predominant NE-SW, NNW-SSE, and ENE-WSW directions (Couto, 1993; Neiva *et al.*, 2008), cutting Cambrian to Carboniferous formations. These mineral deposits formed through the circulation of metamorphic fluids derived from the host metasediments. Variscan folding and thrusting generated shear zones with an anomalous crustal heat flow giving rise

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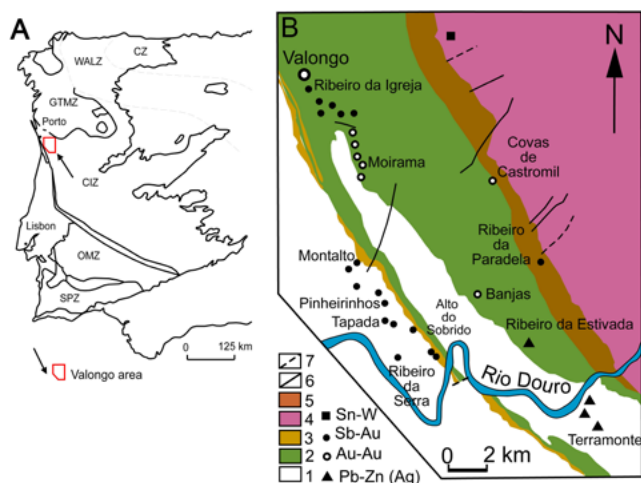


Figure 1. A) Location of Valongo anticline in the map of Portugal and location of geotectonic zones – CZ- Cantabrian Zone; WALZ - West Asturian-Leonese Zone; CIZ - Central Iberian Zone; GTMZ- Galicia Trás-os-Montes Zone; OMZ- Ossa-Morena Zone; SPZ- South Portuguese Zone; B) geological map of Valongo area (adapted from Medeiros, *et al.*, 1964; Medeiros *et al.*, 1980; Couto, 1993); 1- Neoproterozoic-Cambrian Schist-greywacke complex; 2- Ordovician to Devonian; 3- Carboniferous; 4- Variscan (Syn- to late D3) peraluminous two-mica granite and granodiorites; 5- Contact metamorphic aureole; 6- Fault; 7- Probable fault.

Figura 1. A) Localização do anticlinal de Valongo no mapa de Portugal e localização das zonas geotectónicas - CZ - Zona Cantábrica; WALZ - Zona Astúrico Ocidental Leonesa; CIZ - Zona Centro Ibérica; GTMZ - Zona da Galiza Trás-os-Montes; OMZ - Zona de Ossa Morena; SPZ - Zona Sul Portuguesa; B) mapa geológico da área de Valongo (adaptado de Medeiros, *et al.*, 1964; Medeiros *et al.*, 1980; Couto, 1993); 1 - Complexo de Xisto-grauváquico do Neoproterozoico-Câmbrico; 2 - Ordovício a Devoniano; 3 - Carbónico; 4 - Granito e granodioritos de duas micas peraluminosos (sin- a tardi- D3); 5 - Auréola metamórfica de contacto; 6 - Falha; 7 - Falha provável.

to hydrothermal activity (Couto, 1993; Couto *et al.*, 2007; Neiva *et al.*, 2008). The structural control is clear and the Valongo mineral deposits have been associated with shear areas active since the Variscan D1 phase (Pereira *et al.*, 1993).

3. Material and methods

Eight hundred and one stream sediment samples were collected by the consortium Baixo-Douro (EDM-ECD-BRGM) (Viallefond, 1990) at a density of 4 samples/km². The samples were sieved at 125 µm, digested by fusion with sodium peroxide, and analyzed by ICP-AES, with an accuracy of 5-10%. The detection limit for As is 5 ppm. The chemical analyses were carried out by the BRGM laboratory (France).

In geostatistics, the combined effects of different scales of spatial variation of a particular property result in a nested variogram structure. Methods such as Factorial Kriging (Journel *et al.*, 1978; Matheron, 1982; Goovaerts, 1997; Wackernagel, 1998) may then be used to estimate and map individual spatial components of the variogram. The regionalized variable theory (Matheron, 1971, Chiles and Delfiner, 2012) states that a variable in an area has both random and spatial properties that can be characterized by computing an experimental variogram from field sampling, such as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z_{i+h} - Z_i]^2$$

where $\gamma(h)$ is the experimental variogram for the lag distance h between pairs of sampled locations; $N(h)$ is the number of pairs separated by lag distance h ; Z_i and Z_{i+h} are the values of the regionalized variable at the sampled locations i and $i+h$. The experimental variogram can then be fitted by an established model or a linear combination of established models.

Factorial Kriging was utilized for computation. Due to its greater flexibility in modelling different spatial structures — in this case, two isotropic structures at short and long distance (Figura 2) — enabled a reduction in the spatial uncertainty associated with the estimation, compared to Ordinary Kriging. This allowed for a more precise and realistic estimation. The software SpaceStat version 4.1.25, Biomedware, USA, was used for computation.

The As was selected due to its presence in the mineral paragenesis of the Sb-Au and As-Au deposits of the Valongo anticline, as well as being an element that replaces Sb in the stibnite. Stibnite usually contains As (up to 1.39 wt.% As) in the Borrallhal deposit, while in arsenopyrite, Sb replaces As (Couto, 1993; Neiva *et al.*, 2008). The As scores were normal transformed and the kriged values backtransformed to their original units (mg/kg).

4. Results

The variographic study facilitated the identification of two isotropic structures, one at a short range (2 Km) and the other at a long range (7 Km). Two spherical models were applied (Figura 2), with the nugget effect accounting for 49% of the total variance. The remaining 51% was subsequently utilized to create estimated maps for the two identified structures. Factorial kriging was used for separating the short isotropic component from the long isotropic structure. Figure 3 displays the comprehensive estimated map.

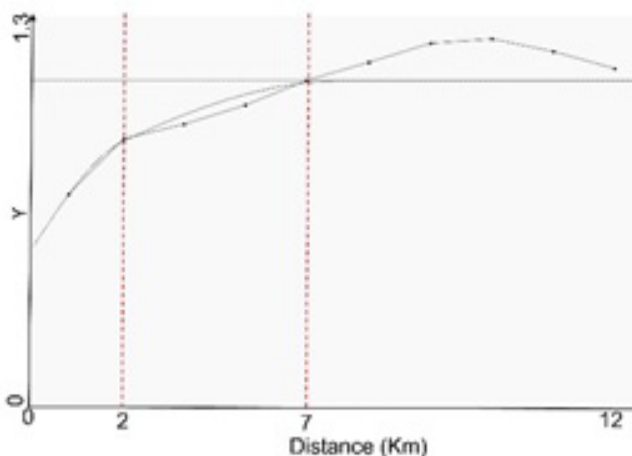


Figure 2. Experimental omnidirectional variogram with the fitting of two spherical models: C0 (nugget effect) = 0,49, C1 (short-distance variance) = 0,19, C2 (long-distance variance) = 0,32, a1 (short-distance range) = 2Km, and a2 (long-distance range) = 7 km.

Figura 2. Variograma experimental omnidirecional com o ajuste de dois modelos esféricos: C0 (efeito de pepita)=0,49, C1 (variância curta distância)=0,19, C2 (variância longa distância)=0,32, a1 (alcance, curta distância)=2Km e a2 (alcance longa distância)=7 km.

5. Discussion

Factorial Kriging holds great promise in identifying preferential directions for future gold exploration in the Valongo region, using arsenic (As) as a proxy. The Valongo area has been historically known

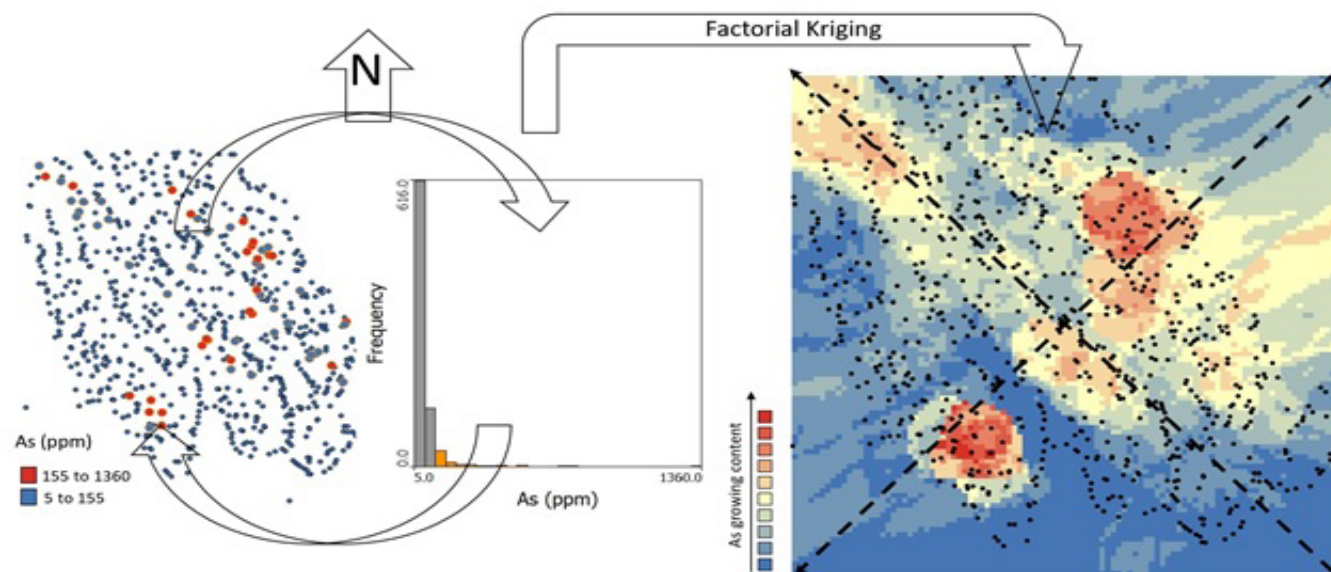


Figure 3. Nested structures along NE-SW and NW-SE directions, As spatial distribution and probable spatial trends.

Figura 3. Estruturas imbricadas ao longo das direções NE-SW e NW-SE, distribuição espacial do As e prováveis direções preferenciais.

for its potential to host valuable mineral deposits, including gold, and employing advanced geostatistical techniques can significantly enhance our understanding of the spatial distribution of mineralizations.

The use of Factorial Kriging takes into account the directional continuity of arsenic concentrations, helping in the definition of the orientations where higher gold mineralization is likely to occur, considering the short (2Km) and long distance (7Km) structures identified in the fitted variograms. The spatial variability of arsenic concentrations in stream sediments is closely associated with certain types of gold mineralization, and its spatial structure may serve as a proxy to potential gold-bearing zones identification.

The results confirmed the previously acknowledged geochemical associations in the stream sediments samples (Carvalho, 2010), namely the identification of NW-SE and NE-SW directions as preferential for the high As content (Figura 2) (Batista *et al.*, 2020; Carvalho, 2020). The results obtained through Factorial Kriging emphasize new As anomalies that are consistent with the location of the Sb-Au and As-Au mineralization (Figura 1B).

The identified preferential directions can guide future prospecting efforts, allowing exploration of areas with the highest likelihood of hosting gold deposits. Furthermore, the incorporation of other geological and structural data, alongside arsenic concentrations, can enhance the accuracy of the exploration targeting, increasing the likelihood of discovering economically viable gold deposits and fostering sustainable mining activities in the area.

6. Conclusions

Factorial Kriging demonstrates significant potential in identifying preferential directions for gold exploration in the Valongo region. By using arsenic as a proxy for gold mineralization, this advanced geostatistical technique helps uncover hidden patterns and structures in the data, guiding future prospecting efforts effectively. The use of Factorial Kriging provided valuable insights into the spatial variability of gold mineralization potential, enabling targeted exploration in areas with a higher likelihood of hosting gold deposits.

The future incorporation of other geological data alongside

arsenic concentrations is an important issue to address in a more comprehensive and less uncertain model. Understanding the geological context is the backbone for interpreting the controls on gold mineralization and the enhancement of the accuracy of exploration efforts.

The application of advanced geostatistical techniques like Factorial Kriging contributes to sustainable mining practices. By pinpointing areas with higher gold mineralization potential, mining activities can be conducted with greater precision, minimizing environmental impact and optimizing resource utilization.

Acknowledgments

This work was supported by GeoBioTec (UIDB/04035/2020) Research Centre, funded by FEDER through the Operational Program Competitiveness Factors COMPETE and by National funds through FCT. The authors are grateful to Laboratório Nacional de Energia e Geologia for providing the data on stream sediments. We thank the anonymous reviewers for the valuable comments that helped improve this manuscript.

References

- Batista, A., Lima, A., Sant'Ovaia, H., 2020. Stream sediments basins applied to metallic elements exploration; a methodological proposal and its applications in gold and antimony exploration in the Dúrico-Beirão District. *Comunicações Geológicas*, **107**, Especial II:63-68.
- Carvalho, P. C. S., 2010. As antigas explorações mineiras de Sb-Au, As-Au e Ag-Pb-Zn a região de Valongo (norte de Portugal): seu impacto ambiental. Faculdade de Ciências e Tecnologia. Universidade de Coimbra. Unpublished PhD. Thesis, Coimbra.
- Carvalho P.C.S., Neiva A.M.R., Silva M.M.V.G., Corfu, F., 2012. A unique sequential melting mechanism for the generation of anatectic granitic rocks from the Penafiel area, northern Portugal, *Lithos*, **155**:110-124.
- Carvalho, A. M., 2020. Geophysical and *Geological Exploration Applied to*

- Sb Mineralizations*. Unpublished Master thesis. Faculdade de Ciências, Universidade do Porto. Porto.
- Couto, H., 1993. *As mineralizações de Sb-Au da região Dúrico-Beirã*. Unpublished PhD thesis. Faculdade de Ciências da Universidade do Porto.
- Couto, H., Roger, G., Borges, F. S., 2007. Late Paleozoic orogenic gold-antimony deposits from the Dúrico-Beirã area (North Portugal): relation with hidden granitic apexes. Proceedings of the Eighth Ninth Biennial Meeting of the Society for Geology Applied to Mineral Deposits, Dublin, Ireland, August 2007. DIGGING DEEPER, *Colin J. Andrew et al. Eds.*, 1:609-612.
- Chilès, J.P., Delfiner, P., 2012. *Geostatistics: Modeling Spatial Uncertainty*. Wiley, New York.
- Goovaerts, P., 1997. *Geostatistics for Natural Resources Evaluation*. Oxford University Press.
- Journel, A.G., Huijbregts, C.J., 1978. *Mining Geostatistics*. Academic Press, London (UK).
- Matheron, G., 1982. *Pour une Analyse Krigeante des données Régionalisées* (in French). Publication N-732, Centre de Géostatistique, Fontainebleau, France.
- Matheron, G., 1971. *The Theory of Regionalized Variables and Its Applications*. École nationale supérieure des mines.
- Medeiros, A. C., Fernandes, A. P., Pilar, L., 1964. *Carta geológica de Portugal. Nota explicativa da Folha 13-B à escala 1/50000*. Serviços Geológicos de Portugal, Lisboa.
- Medeiros, A.C., Pereira, E., Moreira, A., 1980. *Carta geológica de Portugal. Notícia explicativa da folha 9-D à escala 1/50000*. Serviços Geológicos de Portugal, Lisboa.
- Neiva, A. M. R., András, P., Ramos, J. M. F., 2008. Antimony quartz and antimony-gold quartz veins from northern Portugal. *Ore Geology Reviews*, **34**:533-546.
- Pereira, E., Ribeiro, A., Meireles, C., 1993. Cisalhamentos hercínicos e controlo das mineralizações de Sn-W, Au e U da Zona Centro-Ibérica. *Cua. Lab. Xeol. Laxe*, **18**:89-119.
- Viallefond, L., 1990. *Interpretation des resultats de la prospection geochimique tactique de la zone de Tapada-Baixo Douro (Portugal)*. Bureau de recherches geologiques et minières. Orleans.
- Wang, H., Yuan, Z., Cheng, Q., Zhang, S., Sadeghi, B., 2022. Geochemical anomaly definition using stream sediments landscape modeling, *Ore Geology Reviews*, **142**:104715.
- Wackernagel, H., 1998. *Multivariate Geostatistics*. Springer-Verlag.