

Black shales associated with metallic ore deposits in Portugal: a comprehensive petrographic and geochemical study

Vanessa Figueiredo Laranjeira

Doctor's degree in Earth Sciences

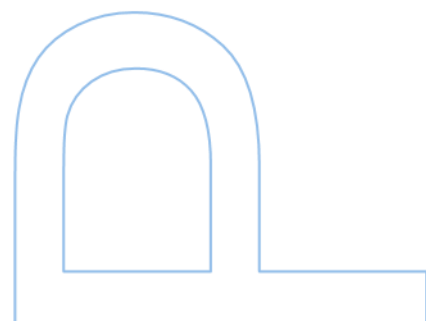
Department of Geosciences, Environment and Spatial Planning
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Supervisor

Doctor Joana Paula Machado Ribeiro, Assistant Professor,
Department of Earth Sciences, University of Coimbra

Co-supervisor

Doctor Deolinda Maria dos Santos Flores Marcelo da Fonseca, Full
Professor, Department of Geosciences, Environment and Spatial
Planning, University of Porto

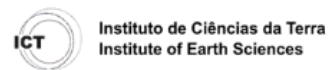


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Vanessa Figueiredo Laranjeira

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To my parents, my grandmother Alice and Victor

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Abstract

Black shales are important in mineralization processes due to the recognize role that the organic matter (OM) may have in transportation, mobilization, deposition, concentration, reduction, and preservation of metals. The occurrence of black shales spatially associated with metal deposits in Portugal is described in the literature. However, the petrographic and geochemical characterization of the organic and inorganic matter in those black shales as well as their association with mineralization processes, were not investigated in detail.

The main objectives of this thesis are: to characterize black shales occurring in Ossa-Morena and Central Iberian geotectonic zones in association to metal deposits, through petrographic, mineralogical, and geochemical methods; and, to contribute to the understanding of their association with those deposits, emphasising the OM.

Samples from outcrops and drill cores from different depths were studied. The methodologies applied for the petrographic, mineralogical, and geochemical studies included: optical microscopy; X-ray diffraction (XRD) analysis; scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX); determination of total organic carbon and total sulphur by LECO analyser; and, inductively coupled plasma emission spectrometry/mass spectrometry (ICP-ES/MS). The comparison of the chemical composition of the studied black shales with reference values, statistical analysis, calculation of Pearson correlation coefficients, and calculation of ratios between redox sensitive elements supported the data analysis.

The petrographic observations of black shales allowed the identification of organic particles with variable size and shape, occurring interbedded along mineral matter. Some samples showed vitrinite-like particles exhibiting graphitic features and fragments of zooclasts (some identified as graptolites). The maturation of the OM and the estimation of paleotemperatures were obtained through measurement of random and maximum reflectance of organic particles. The results indicated maturation ranging between anthracite and semi-graphite. The variation of OM maturation evidences the influence of hydrothermal fluids and metamorphic/metasomatic processes in the studied areas.

The geochemical analyses, comprising the determination of chemical composition, integrated with SEM-EDS and mineralogical results, provided information about elements association and modes of occurrence, and about paleodepositional conditions.

The Precambrian black shales from the *Série Negra* succession in Ossa-Morena Zone have organic particles with variable abundance, size and shape, and the reflectance indicates that the OM maturation is classified as anthracite to semi-graphite. Considering the depositional paleoenvironment, the anoxic conditions were predominant, favoring OM preservation and the accumulation of some metals. The elements Ag, Cd, Cu, Pb, and Se are preferentially associated with sulfides, whereas Mo and U are preferentially organically bounded. The results reveal that the black shales from the *Série Negra* succession in Ossa-Morena Zone may represent a source of metals, probably remobilized during Variscan events.

The Silurian black shales from *Xistos com Nódulos* Formation in Ossa-Morena Zone present vitrinite-like particles in all samples (with variable abundance) and remains of graptolites in some of the them. The redox sensitive elements indicate deposition under suboxic to anoxic conditions. Geochemical data indicate that the enrichment of some metals in black shales, including Cu, is related with post-depositional processes. The variation of thermal maturation registered in the OM can be interpreted as a result of the hydrothermal activity and the pathway of hydrothermal fluids. The regional thermal evolution shows a spatial architecture compatible with the existence of a deep-seated magmatic body, emplaced during late Variscan stages, that may have generated magmatic-derived hydrothermal fluids.

The Cambrian black shales from *Bateiras* Formation in Central Iberian Zone include scarce and small organic particles, with some exhibiting graphitic structure. The maturation of OM ranges from anthracite to meta-anthracite. Oxidizing conditions and terrigenous sources of sediments were predicted regarding the paleoenvironment of the studied black shales. The variation of the maturation is related with metamorphic/metassomatic processes associated with skarns formation. The enrichment and mode of occurrence of some elements are explained by the involvement of granitic rocks installation and related fluids.

Resumo

Os xistos negros são importantes em processos de mineralização devido ao reconhecido papel que a matéria orgânica pode ter no transporte, mobilização, deposição, concentração, redução e preservação de metais. A ocorrência de xistos negros espacialmente associados a depósitos metálicos em Portugal está descrita na literatura. No entanto, a caracterização petrográfica e geoquímica da matéria orgânica e inorgânica nesses xistos negros, assim como a sua associação à génese de depósitos, não foram investigados em detalhe.

Os principais objetivos desta tese são: caracterizar os xistos negros presentes nas zonas geotectónicas de Ossa-Morena e Centro Ibérica, em associação com os depósitos metálicos, através de métodos petrográficos, mineralógicos e geoquímicos; e contribuir para a compreensão da sua associação a esses depósitos, com ênfase na matéria orgânica.

Foram estudadas amostras de afloramentos e de testemunhos de sondagens, de diferentes profundidades. As metodologias utilizadas nos estudos petrográficos, mineralógicos e geoquímicos incluíram: microscopia ótica; análise de difração de raios-X (XRD); microscopia eletrónica de varrimento com espectrometria de raios-X por energia dispersiva (SEM-EDX); determinação de carbono orgânico total e enxofre total através de analisador LECO; e espectrometria de massa/emissão acoplada a plasma indutivo (ICP-ES/MS). A comparação da composição química dos xistos negros estudados com valores de referência, análise estatística, cálculo de coeficientes de correlação de Pearson e cálculo de razões entre elementos sensíveis a condições paleo-redutoras suportaram a análise de dados.

As observações petrográficas dos xistos negros permitiram a identificação de partículas de matéria orgânica com tamanho e formas variáveis, ocorrendo intercaladas com a matéria mineral. Algumas amostras apresentaram partículas orgânicas com características grafitosas e fragmentos de zooclastos (alguns identificados como graptólitos). A maturação da matéria orgânica e a estimação de paleotemperaturas foram obtidas através da medição de refletância média e máxima de partículas orgânicas. Os resultados indicaram um grau de maturação entre antracite e semi-grafite. As variações na maturação da matéria orgânica evidenciam a influência de fluidos hidrotermais e de processos metamórficos/metassomáticos nas áreas estudadas.

A análise geoquímica, incluindo a determinação da composição química, integrada com os resultados de SEM-EDX e mineralogia, forneceram informações sobre a associação de elementos e modo de ocorrência, e sobre condições paleo-deposicionais.

Os xistos negros do Pré-Câmbrico pertencentes à Série Negra da Zona Ossa-Morena têm partículas orgânicas com abundância, tamanhos e formas variáveis, e a refletância indica que a matéria orgânica corresponde a antracite, meta-antracite e semi-grafite. Considerando o paleoambiente deposicional, registou-se o predomínio de condições anóxicas, favorecendo a preservação da matéria orgânica e a acumulação de alguns metais. Os elementos Ag, Cd, Cu, Pb e Se estão preferencialmente associados a sulfuretos, enquanto o Mo e U estão preferencialmente associados à matéria orgânica. Os resultados revelam que os xistos negros da sucessão Série Negra da Zona Ossa-Morena podem representar uma fonte de metais, provavelmente remobilizados durante eventos Variscos.

Os xistos negros do Silúrico pertencente à Formação Xistos com Nódulos da Zona de Ossa-Morena apresentam partículas orgânica em todas as amostras (com abundância variável), identificando-se restos de graptólitos em algumas delas. Os elementos sensíveis a condições redutoras indicam deposição em condições sub-óxicas a anóxicas. Os dados geoquímicos indicam que o enriquecimento de alguns metais, incluindo o Cu, nos xistos negros está relacionado com processos pós-deposicionais. A variação da maturação térmica registrada na matéria orgânica pode ser interpretada como resultado da atividade hidrotermal e da trajetória dos fluidos hidrotermais. A evolução térmica regional demonstra uma arquitetura espacial compatível com a existência de um corpo magmático profundo, localizado durante a fase Varisca tardia, que pode ter gerado fluidos hidrotermais de origem magmática.

Os xistos negros do Câmbrio da Formação de Bateiras da Zona Centro Ibérica apresentam partículas orgânicas com tamanho e forma variáveis, com algumas partículas exibindo estrutura grafítica. A maturação da matéria orgânica varia de antracite a meta-antracite. Condições oxidantes e fontes terrígenas foram determinadas em relação aos paleoambientes de formação dos xistos negros estudados. A variação da maturação está relacionada com processos metamórficos/metassomáticos associados à formação de skarns. O enriquecimento e o modo de ocorrência de alguns elementos são explicados pelo envolvimento da instalação de rochas graníticas e fluidos relacionados.

Contribution of Co-authors

Joana Ribeiro (Department of Earth Sciences, University of Coimbra and Instituto Dom Luiz), as thesis supervisor, assisted and supported all work developed for this thesis.

Deolinda Flores (Institute of Earth Sciences - Pole of University of Porto and Department of Geosciences, Environment and Spatial Planning, Faculty of Sciences, University of Porto), as thesis co-supervisor, assisted all work developed for this thesis.

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CHAPTER 1

INTRODUCTION

1.1. Subject

Black shales are defined as fine-grained rocks with organic matter (OM), where the total organic carbon (TOC) is above 0.5 wt.% (Huyck, 1989; Trabucho-Alexandre, 2014); and they are the result of the accumulation and preservation of OM in the sediments mostly under reducing conditions (Tourtelot, 1979; Wignall, 1994). Black shales are generally formed in marine anoxic bottom waters, although they can occur in a wide range of depositional environments (e.g., Schieber, 1978; Potter et al., 1980; Gao et al., 2016; Ai et al., 2020).

The long-established term black shale has been used for a wide variety of rock types in the literature, commonly without any specific definition (Wignall, 1994). It has long been recognized that the definition of the term black shale is not precise since it does not fulfil the requirements as might be set forward by the several geologists who often use the term (Swanson, 1961). However, over the years, various definitions have emerged. Black shales are most often described as argillaceous, argillaceous-pelitic, argillaceous-siliceous and argillaceous-carbonate sediments with higher amounts of more or less preserved OM responsible for the black or dark grey color of these rocks (e.g., Leventhal, 1993; Nowak, 2007). Inconsistencies, some of them eventually related to translations, are found in the bibliography, confusing black shales and black schist. The term black shale is often used to describe metamorphosed rocks. Some studies related to Ossa-Morena Zone and the Central Iberian Zone refer to the term black shales, even when metamorphosed formations are described (e.g., Sousa, 1982; Sousa and Sequeira, 1989; Oliveira et al., 1991; Tornos et al., 2004; Araújo et al., 2013; Quesada and Oliveira, 2019). Considering the inconsistencies in the bibliography, including scientific publications and reports from exploration companies, the term black shales will be used in this work.

The occurrence of black shales is common and widespread in the geological record (Tourtelot, 1979; Sozinov, 1982; Wignall, 1994; Kunzmann et al., 2015; Wang et al., 2019). Black shales are significant in economic geology since they can be the source rock for hydrocarbons production and are often spatially associated with several types of ore deposits, mostly due to the enrichment of metals within black shales successions (e.g., Potter et al., 1980; Sozinov, 1982; Cortial et al., 1990; Sáez et al., 2011; Suárez-Ruiz et al., 2012; Kontinen and Hanski, 2015; Gao et al., 2016). Black shales, due to the active participation of the OM, provide the necessary redox conditions for an enrichment of metals in the sediments. Therefore, these rock units are a valuable source of metals

for later mineralizing processes (Sozinov, 1982; Suárez-Ruiz et al., 2012 and references therein).

Numerous metal-rich deposits are related with host rocks that have a high concentration of organic carbon, such as black shales, suggesting that OM is somehow implicated with the metallogenic mechanisms, playing a role in the deposition and concentration of metals. Another hypothesis is that the rocks are themselves a source of metals that can be remobilized and concentrated elsewhere (Leventhal, 1986; Maynard et al., 2001; Coveney and Pašava, 2004; Greenwood et al., 2013; Wang et al., 2022). Black shales are being investigated worldwide because their relation with hydrocarbon generation potential, as well as spatial association with several metal deposits (e.g., Au, Ag, Co, Cu, Hg, Mo, Ni, Mn, Sb, V, U, Zn, W, PGE and others) (e.g., Vine and Tourtelot, 1970; Wignall, 1994; Coveney and Pašava, 2004).

It can be found in the literature a great number of studies about metal-enriched black shales and the participation of OM in ore formation. Some associations are reviewed for example, in: Pb and Zn ores of the American Mississippi Valley including the Viburnum Trend, the world's largest known concentration of Pb, that occur on the peripheries of basins containing hydrocarbon deposits and black shales (Anderson and Macqueen, 1982; Spirakis and Heyl, 1988; Rimmer, 2004); sediment-hosted Mn deposits associated with black shales in the Eastern Carpathian Mountains of Romania (Munteanu et al., 2003); Kupferschiefer in Central Europe hosts the Cu-Pb-Zn-S mineralization with noble metals (Borg et al., 2012; Alderton et al., 2016); giant Au-PGE lode deposit hosted by metamorphosed black shales at Sukhoi Log in Siberia (Distler et al., 2003); black shales of the Lower Cambrian Niutitang Formation in southern China host regionally distributed stratiform polymetallic Ni-Mo-platinum group elements (PGE)-Au phosphate and sulfide-rich ores (Pasava et al., 2008); the OM (kerogen and bitumen) occurs with Au and uraninite in the Witwatersrand ore deposits in South Africa (Mossman et al., 2008); bitumen associated with Cu deposits in Chile (Cisternas and Hermosilla, 2006); Sn polymetallic sulfide deposits in Devonian black shales of the Dachang area in South China, among others (e.g., Glikson and Mastalerz, 2000; Coveney and Pasava, 2004; Uffmann et al., 2012; Loukola-Ruskeeniemi and Lahtinen, 2013; Baioumy et al., 2016).

Some studies also describe the association of carbonaceous shales or graphitic shales with skarn deposits, such as, Changlongshan Fe-skarn deposit located in the northeastern part of the Tongling-Fanchang Fe-Cu district, China (Xu and Lin, 2000); Jiama Porphyry-Skarn deposit with Cu, Mo, Pb and Zn (Au) in China (Zheng et al., 2016); Hämmerlein polymetallic skarn deposit in Germany (Lefebvre et al., 2018); San Miguel

skarn of Tandilia Belt (Argentina) (Lajoinie et al., 2019); Yaojialing Zn skarn polymetallic deposit in China (Xiong et al., 2022).

Black shales may behave as host rocks for metal deposition or can be the source of metals that concentrate elsewhere (Coveney and Pašava, 2004). Usually, metals are transported in hydrothermal fluids to a location where deposition occurs, as response to physicochemical variations of the environment or of the fluid itself (Meyers et al., 1992). The metallic enrichment can result from redox reactions facilitated by bacteria during early diagenesis and also can be associated with post-diagenetic hydrothermal processes after deep burial evolution (Meyers et al., 1992). The continued inflow of metal bearing solutions can lead to the deposition of substantial amounts of metalliferous minerals, and, in favorable conditions, this enrichment generates an ore deposit (Meyers et al., 1992). The OM may have an active role in numerous processes related to the ore deposit genesis, namely (Leventhal, 1986; 1993; Meyers et al., 1992; Suárez-Ruiz et al., 2012): in transportation, mobilization, deposition, concentration, reduction, and preservation.

Mossman (1999) confirmed that the OM may concentrate metals through elemental accumulation in living organisms (biomineralization processes), metal absorption, and OM facilitation of reduction reactions through electron donation (Suárez-Ruiz et al., 2012). Organic matter interacts with metals due to their inherent reducing, acidic and chelating properties (e.g., Disnar and Sureau, 1990; Mossman, 1999). The redox reactions are also important mechanism in diagenetic and epigenetic ore forming environments wherein OM acts as a reducing agent for example for soluble metal sulfates in the generation of metal-sulfide deposits and/or the reduction of soluble metal cations to the insoluble native element (e.g., Disnar and Sureau, 1990; Mossman, 1999 *in* Suárez-Ruiz et al., 2012).

The study of OM rich rocks can be used to understand the metallic ore concentration and, consequently, the processes related to ore deposit genesis (Suárez-Ruiz et al., 2012). The detailed characterization of the OM supports the evaluation of the time-temperature history either in ores or host rocks, once reflectance of the organic particles increases with thermal maturation through burial, hydrothermal or magmatic activity (e.g., Eakin and Gize, 1992; Landais, 1993; Macqueen, 1984 *in* Suárez-Ruiz et al., 2012). These studies also reveal the active or passive role that OM plays in ore formation, thereby helping to determine the source of metals, transportation, and precipitation mechanisms (Suárez-Ruiz et al., 2012). Key parameters to be analyzed in the OM occurring in association with ore deposits are the source and type of OM, its

thermal evolution (maturation) and spatial variation, hence, identifying possible thermal anomalies (Gize, 1993; Suárez-Ruiz et al., 2012). These parameters can be assessed by petrographic techniques, including the analysis of the reflectance of OM that is useful to assess paleotemperatures. Vitrinite reflectance is widely used and a robust thermal maturity parameter (Tissot and Welte, 1984; Hunt, 1996; Hackley et al., 2009). However, Pre-Devonian rocks do not contain vitrinite, because it is originated from vascular land plants that postdated the Late Silurian times (Tissot and Welte, 1984; Taylor et al., 1998); nevertheless, the reflectance of other organic components, namely faunal remains, are used to quantify the thermal maturation of sequences of this age (Hartkopf-Fröder et al., 2015).

The combination of organic petrographic methods with geochemical analysis allows the characterization of the source, type, and maturation of OM, and to identify the active or passive role in the concentration of metals in a specific ore deposit (Suárez-Ruiz et al., 2012). The geochemical analysis of organic and inorganic fractions provides further information on elements concentration, depositional environment, migration pathways of hydrothermal fluids and can contribute to the knowledge of mineralization processes (Tissot and Welte, 1984; Peters et al., 2005; Greenwood et al., 2013).

Therefore, the use of geochemical proxies allows the characterization of paleodepositional environments at the time of sedimentation and diagenesis (e.g., Gao et al., 2016; Fang et al., 2019). The redox variations are mainly controlled by the availability of O_2 and H_2S , represented essentially by the presence of OM, sulfides and biological activity (e.g., Jones and Manning, 1994; El-Anwar et al., 2018; Ferreira et al., 2020) and can be evaluated based on the relationships between some trace elements, namely As, Cr, Co, Cu, Mo, Ni, U, V (Leventhal, 1993).

In Portugal, is identified and described in the geological cartography the existence of various occurrences of black shales, and part of them are spatially associated with ore deposits in different geotectonic zones (Oliveira et al., 1992; Dias et al., 2013 and references therein). The petrography and geochemistry of the organic and inorganic matter present in these black shales, together with their association with metal deposits, particularly the role of OM in the mineralization mechanisms, were never investigated in detail.

1.2. Objectives

The main goal of this research is the systematic investigation of black shales occurrences in Portugal, specifically in Ossa-Morena Zone (OMZ) and Central Iberian Zone (CIZ), and the establishment of their interplay with mineralizations spatially associated, emphasizing the role of OM in ore forming processes.

The specific objectives are as follow:

- (i) to determine the total organic carbon in the black shales;
- (ii) to characterize the OM present in the black shales for identification of type and source of OM and determination of thermal maturation;
- (iii) to determine the geochemical composition of the black shales, including the determination of elements concentration and mode of occurrence;
- (iv) to identify mineral constituents and their mode of occurrence in the black shales;
- (v) to establish the relationship between the organic and mineral matter in the black shales;
- (vi) to recognize and describe the role of the black shales in the ore-forming processes in spatially related metal ore deposits.

The strategy for the research implementation and development included:

- Systematic identification of black shales occurrences in Portugal and selection of black shales to be investigated based on the literature, cartography, and in the know-how existing among other researchers;
- Development of field work to identify the selected black shales formations and for samples collection (in outcrops and drill cores);
- Comprehensive characterization of black shales using a multi-analytical approach to obtain the data needed to fulfill the defined objectives.

1.3. Thesis structure

This thesis is presented in research articles-based format, comprising scientific articles (published and submitted for publication), that are framed and integrated. In this context, the thesis is composed of six chapters.

Chapter 1 includes a general introduction which outlines the subject and objectives, as well as an overview about the investigated materials and the applied methodologies. The information presented herein frames the next chapters that include the results (chapters 2, 3, and 4, based on published and submitted for publication research articles).

Chapter 2 describes the results obtained for Precambrian black shales from Ossa-Morena Zone, which comprises one scientific research article (published in an international peer-reviewed journal) and one book chapter (accepted for publication).

Chapter 3 refers to the study of Silurian black shales from Ossa-Morena Zone spatially associated to Cu deposits, through one scientific research article (accepted for publication in an international peer-reviewed journal).

Chapter 4 is about the study of Cambrian black shales spatially associated to W-skarns, in the Central Iberian Zone, which includes one scientific research article (submitted for publication in an international peer-reviewed journal).

Chapter 5 includes the general conclusions of the presented research, systematizing the most important findings, and the identification of some topics that emerged from the investigation for future research.

Chapter 6 presents an atlas based on photomicrographs obtained during the observations under the microscope to show the petrographic characteristics of the OM in the studied black shales. Some of the presented images are mosaics obtained from the assembling of photomicrographs. This section is sub-divided in three parts in accordance with the case studies, this is, the Precambrian, Silurian, and Cambrian black shales.

The publications in which this thesis is based are the following:

Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., Mendonça Filho, J. G., Flores, D., 2023. Petrographic and geochemical characterization of organic matter of Precambrian black shales from Ossa-Morena Zone, South of Portugal. *In*: Chaminé, H. I., Fernandes, J.A. (Eds.), *Advances in Geoengineering, Geotechnologies, and Geoenvironment for Earth Systems and Sustainable Georesources Management: Proceedings of the 1st Conference on Georesources, Geomaterials, Geotechnologies and Geoenvironment*. Springer ASTI. https://doi.org/10.1007/978-3-031-25986-9_16.

Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., Flores, D., 2023. Geochemistry of Precambrian black shales from Ossa-Morena Zone (Portugal): depositional environment and possible source of metals. *Journal of Iberian Geology*. <https://doi.org/10.1007/s41513-022-00202-6>.

Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., Mendonça Filho, J. G., Rocha, F., Flores, D., 2023. Silurian black shales from Sousel-Barrancos Metallogenic Belt (Ossa-Morena Zone, Portugal): characterization and interplay to Cu deposits. *International Journal of Coal Geology*. <https://doi.org/10.1016/j.coal.2023.104253>.

Laranjeira, V., Ribeiro, J., Mendonça Filho, J. G., Flores, D. (submitted). Black shales spatially associated to a W-Skarn deposit from Douro Scheelite Belt (Portugal): insights from petrographic and geochemical studies.

1.4. Investigated black shales

Several occurrences of black shales in Portugal were identified (Oliveira et al., 1992; Dias et al., 2013 and references therein), but scarce references about the comprehensive petrographic and geochemical characterization of OM are found (e.g., Chaminé et al., 2003; Flores et al., 2010). Despite the existence of several occurrences of black shales in Portugal in spatial association with metal deposits, they have not yet been investigated in detail for their relationship and metallogenic potential. In this context, the comprehensive characterization, including petrographic, mineralogical, and geochemical multi-analytical approach, of both organic and inorganic matter in black shales, can provide valuable knowledge about the general characteristics of black shales formations and contribute to the understanding of geological mechanisms that lead to the accumulation of metals in association with black shales.

The black shales occurrences selected for investigation in this research include black shales from Ossa-Morena Zone (OMZ) and Central Iberian Zone (CIZ). These black shales occurrences were selected based on the following criteria: (i) they are related to deposits that were recent targets of geological exploration by private companies; (ii) the possibility to have access to samples from drill cores; (iii) the know-how available and recently produced; (iv) they represent different ages and Portuguese geotectonic zones.

1.4.1. Black shales from Ossa-Morena Zone - occurrences in Sousel-Barrancos metallogenic zone

Precambrian black shales from *Série Negra* succession

Several studies on Precambrian black shales have demonstrated their relevance on the recognition of paleogeographic conditions, depositional environments, processes affecting metamorphic complexes, as well as in ore deposits genesis (e.g., Sozinov, 1982; Kunzmann et al., 2015; Fang et al., 2019). The main sources of OM in Ediacaran rocks have been interpreted as result from the accumulation of prokaryotic (e.g., bacterial) and eukaryotic (e.g., algal) organisms (Ai et al., 2020).

Precambrian successions with black shales, specifically from the Ediacaran, occur in the southernmost tectonostratigraphic zone of Iberian Terrane, the OMZ, locally named the *Série Negra* succession (e.g., Carvalhosa, 1965; Gonçalves and Oliveira, 1986; Oliveira et al., 1991; Gonçalves and Carvalhosa, 1994). Previous investigations addressed its paleogeography, based on the petrographic and geochemical characterization of the

inorganic fraction of the different lithologies of the Precambrian of OMZ, including the *Série Negra* succession (e.g., Oliveira et al., 2003; Pereira et al., 2006; López-Guijarro, 2006; Chichorro et al., 2008; López-Guijarro et al., 2008; Lopes, 2015; Lopes et al., 2015). However, the black shales from the *Série Negra* were never investigated in detail, principally regarding the OM. The first approach to the characterization of the OM present in the black shales from the *Série Negra* was recently published by Laranjeira et al. (2023), where the petrographic observation allowed the identification of OM exhibiting graphitic features, disseminated as flakes in association with iron oxides.

Considering the importance of black shales for paleoenvironmental studies and its potential association with the genesis of ore deposits, this work is a contribution to the knowledge of the Ediacaran black shales from *Série Negra* of OMZ, discussing its organic content and geochemical features, establishing the depositional paleoenvironmental conditions and the sedimentary sources based on geochemical proxies. Moreover, the role of these black shales as a possible source of metals is discussed.

Silurian black shales from *Xistos com Nódulos* Formation

In central OMZ, namely in Sousel-Barrancos metallogenic belt, several Cu-Fe ($\pm$ Zn $\pm$ Pb $\pm$ Au) vein occurrences and deposits are known, that share common features. The Cu-Fe veins are composed of quartz-carbonate and sulfides, being hosted in Paleozoic metasedimentary series (Mateus et al., 2003; 2013; Maia et al., 2019; 2020). Several of these Cu-Fe veins were object of exploitation, during the 19th and 20th centuries (e.g., Oliveira, 1984; 1986; Matos and Rosa, 2001; Mateus et al., 2003; 2013; Tornos et al., 2004). In the Sousel-Barrancos metallogenic belt, there are two important clusters of Cu occurrences: (1) Alandroal cluster, where the Bugalho, Zambujeira, Miguel Vacas and Mociços mines are located; and (2) Barrancos cluster, where the Minancos, Aparis, Botefa and Defesa das Mercês mines are placed (Matos and Filipe, 2013; Mateus et al., 2013).

The veins cut the Paleozoic metasedimentary successions, namely Ordovician to Lower Devonian units. Nevertheless, most of veins are hosted in black to grey shales, sometimes with interbedded lydites and black quartzites (Oliveira, 1986; Mateus et al., 2013) of Silurian to Lower Devonian age (*Xistos com Nódulos* and *Xistos Raiados* Formations). The presence of disseminated pyrite is also a common feature on the Silurian black shales (Oliveira, 1986).

This research aims to explore the relationship between Silurian black shales and spatially associated Cu mineralizations, with a focus on the role of OM in ore forming processes of the OMZ. For this, the specific objectives are: identify type, source, and maturation of the OM by petrographic analyses; and determine the geochemical composition of black shales to explore elements concentration, mode of occurrence and paleodepositional conditions of the Silurian black shales.

1.4.2. Black shales from Central Iberian Zone - occurrence in W-skarns in Vila Seca-Santo Adrião deposit

Cambrian black shales from *Bateiras* Formation

Skarns are defined as metamorphic rocks with granoblastic texture, and a calc-silicate mineral assemblage usually dominated by garnet and pyroxene (Einaudi et al., 1981; Meinert, 1992) and can form by metasomatic processes at the contact of an intrusion, most often acidic or intermediate, with carbonate-bearing rocks (e.g., limestone, dolomite, marble, marl). Other authors referred that skarns can be the result of the transformation of pre-existing rocks, independently of the composition of the protolith, during the regional or contact metamorphism processes, by metasomatic processes that could involve magmatic-, metamorphic-, meteoric- and/or with marine-derived fluids (Meinert, 1992; Meinert et al., 2005).

The skarn evolution is characterized by different stages (Einaudi et al., 1981; Kwak, 1987): stage 1 - isochemical metamorphism - metamorphic recrystallization and mineralogical changes occur, which form calcosilicate minerals and includes development of marble, cornea, quartzite, reaction skarn, skarnoid, talc and wollastonite towards the periphery; the mineral assemblage reflects the composition of the protolith and the alteration is largely a thermal effect but fluids likely circulate due to dehydration reactions; stage 2 - prograde metasomatism and replacement (infiltration) with higher temperatures (800 °C to 400°C; Kwak, 1986) - that involves a hydrothermal fluid (in faults, joints, bedding) and the metasomatic minerals are similar to previous stage but more pervasive and coarse-grained replacing earlier formed assemblages; stage 3 - retrograde metasomatism and replacement (infiltration) - cooling of the pluton and circulation of water temperatures lower than the previous stage, hydrated minerals are formed from previously formed anhydrous minerals, including epidote, actinolite, chlorite and others; there is a structural control and an overlap to the prograde sequence.

Skarns can host ore deposits, as Sn, W, Fe, Cu, Mo, Zn-Pb and Au. These mineralizations can be explained by the different compositions, oxidation states and the metallogenic affinity of the protolith (Einaudi et al., 1981; Meinert et al., 2005). Different types of skarns deposits can be classified by their dominant economic element: Fe skarns, Au and W skarns to Sn-W-Zn-Pb-Cu skarns, among others (Bonewitz, 2012). W-skarn deposits contain mostly scheelite (tungsten), molybdenite, Cu-Fe sulfide, and chalcopyrite (Haldar, 2020). These skarns are emplaced in a generally deeper, higher temperature and more reduced environment (Dawson, 1996). Scheelite is often temporally and spatially related to the growth of certain silicate minerals (e.g., vesuvianite and garnet) and accessory halides, phosphates, and oxide minerals, which sequentially provide important insights into both the genesis of scheelite and the dissolution-precipitation processes of W during metasomatism (Auwera and Andre, 1991; Aksyuk, 2000; Singoyi and Khin Zaw, 2001; Rasmussen and Mortensen, 2013 in Guo et al., 2016).

The CIZ host most of the W-Sn deposits in Portugal, found in vein-type systems (e.g. Panasqueira), stock works, greisen, and in skarn - stratoid type (e.g., Tarouca). W-skarns have also been identified, as is the case of Vila Seca-Santo Adrião. Coelho (1990) studied the W ore deposit with bedrock calcic skarn that incorporates the principal host mineral of W, scheelite, from Covas, in Vila Nova de Cerveira also located in CIZ. W-Sn skarns deposits occurs in the so-called Douro Scheelite Belt (DSB) (Goinhas, 1985; Martins, 2012) characterized by the contact between the metasedimentary formations of lower Cambrian, and the Variscan syn-orogenic granites (Sousa, 1982). In this context, the CIZ is characterized by one of the most important metallogenic W-Sn provinces of Europe (Golder Associates, 2020).

Previous investigations identified the occurrence of black shales in the vicinity of the W-skarns from Vila Seca-Santo Adrião deposit in CIZ (e.g., Sousa, 1982; Sousa and Sequeira, 1989). As far as known from bibliography, the detailed investigation on the association between the W-skarn deposits and black shales, including the petrographic characterization of the OM, is yet to be developed in Vila Seca-Santo Adrião deposit. Foucaud et al. (2018) stated that the black shales occurring in the vicinity of the Tabuaço deposit (Aveleira and São Pedro das Águas), close to the area under study, may have contributed to the formation of pyrite and garnet. This research aims to contribute to the knowledge about black shales from Bateiras Formation (from Cambrian) and related W-skarns in Vila Seca-Santo Adrião deposit, based on the petrographic and geochemical characterization of the organic and inorganic matter present in selected black shales.

1.5. Methodologies

Samples of black shales were selected and collected from outcrops and drill cores, and subsequently carried to the laboratory for preparation. In laboratory, the samples were dried and, before crushing, a representative solid piece of about 30 to 40 mm² of each sample was selected for petrographic observations. Then, the samples were crushed to 1 mm, homogenized, and quartered to get representative portions for petrographic analysis (< 1 mm) and geochemical analysis (crushed to < 212 µm).

Polished blocks for petrographic analysis were done with both, the rock fragments, and the crushed samples in accordance with ISO standard (ISO 7404-2, 2009). The petrographic characterization through optical microscopy allowed the identification and characterization of the OM and the measurement of mean and maximum random reflectance of organic particles. The mean and maximum random reflectance (R_r and R_{max} , respectively) were measured following ASTM D7708-14 (2014). This standardized protocol refers that at least 20-30 particles should be measured; however, in some of the studied samples, it was not possible to find the minimum number of organic particles. The polished blocks of solid pieces were useful to identify the association and modes of occurrence of the petrographic components, which may not be observable after crushing, and provide support for the interpretation of mineralogical and geochemical data.

The petrographic observations and measurements were carried out using a Leica 4000 M microscope equipped with a Discus-Fossil system and with a 50x immersion oil objective. In each prepared block (crushed sample and solid piece) mosaics were made by assembling photomicrographs obtained from the successive sweeping with simultaneous acquisition of photomicrographs along the surface of the polished blocks, using the 20x immersion oil objective. The obtained mosaics in this study have 30 to 200 photomicrographs.

The geochemical characterization included the determination of total organic carbon (TOC) and total sulfur (TS) using a LECO SC 144 analyzer after samples acidification, following NCEA-C-1282, EMASC-001 (US - EPA, 2002) and ASTM D 4239-08 (2008) standards. The TOC and TS analysis was carried out at Palynofacies and Organic Facies Laboratory (LAFO), Federal University of Rio de Janeiro (Brazil). The concentration of major and trace elements was determined using inductively coupled plasma emission spectrometry/mass spectrometry (ICP-ES/MS) after digestion with an acid solution of H₂O-HF-HClO₄-HNO₃, in Bureau Veritas Mineral Laboratories (Canada). Analysis of reference materials, duplicates and blanks was performed for quality assurance.

In selected samples, the X-Ray Diffraction (XRD) analysis was accomplished to support the mineral identification. The mineralogical composition was established by XRD with Cu-K α radiation, using a Malvern Panalytical Phillips X'Pert PW3040/60 equipped with X'Pert 2.0 and Profit software at the Central Analysis Laboratory of the Department of Geosciences in the University of Aveiro (Portugal).

Scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX) analyses were also performed in selected samples to investigate the mineralogical constituents based on qualitative chemical compositions and the elements mode of occurrence. The observations under secondary electrons and back scattered electrons detection modes on the polished blocks were performed with an FEI Quanta 400FEG environmental SEM, equipped with a Genesis X4M energy dispersive X-ray analyzer in Materials Centre of the University of Porto (Portugal).

The chemical composition of the studied black shales was compared with reference values reported for Background of Black Shales (BBS) (Ketris and Yudovich, 2009); and in some samples also with North American Shale Composition (NASC; Gromet et al., 1984; Taylor and McLennan, 1985; Condie, 1993); Post Archean Australian Shale (PAAS; Taylor and McLennan, 1985; Condie, 1993); Average Shale (AS; Wedepohl, 1971; Piper, 1974); and, Upper Continental Crust (UCC; Rudnick and Gao, 2014).

The enrichment/depletion behavior of elements was determined relatively to the reference values through calculation of concentration coefficients (CC). The CC were calculated through the ratio between elements concentration in the studied samples and their concentration in reference data and provides information about the depletion ($CC < 1$) or enrichment ($CC > 1$) of elements. The CC allows the classification of the enrichment of elements according with Dai et al. (2016) as: significant enriched when $CC > 10$; slightly enriched when $2 < CC < 10$, normal when $1 < CC < 2$; and depleted when $CC < 0.5$.

The Pearson correlation coefficients were calculated to investigate elements affinity, supporting the identification of modes of occurrence. The ratio between redox sensitive elements were calculated to obtain information regarding depositional conditions and differences amongst the studied black shales (e.g., Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer, 2004; Tribouillard, 2006; Ross and Bustin, 2009).

CHAPTER 2

PRECAMBRIAN BLACK SHALES FROM OSSA- MORENA ZONE

Petrographic and geochemical characterization of organic matter of Precambrian black shales from Ossa-Morena Zone, South of Portugal.

Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., Mendonça Filho, J., Flores, D., 2023.

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Geochemistry of Precambrian black shales from Ossa-Morena Zone (Portugal): depositional environment and possible source of metals.

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Journal of Iberian Geology. <https://doi.org/10.1007/s41513-022-00202-6>.

Abstract

Black shale lithologies are represented in Precambrian (Ediacaran) of Ossa-Morena Zone, SW of Iberian Massif, through the *Série Negra* lithological succession. The investigation on the OM in black shales is relevant to understanding the mechanisms and depositional paleoenvironments related to that genesis. Therefore, the paleodepositional environments related these rocks were investigated using their geochemical composition to identify the sedimentary sources and depositional conditions. Their potential for assisting the genesis of metal deposits was also discussed. The petrographic study allowed the identification of organic particles with variable abundance, size and shape in all samples. The maximum reflectance indicates that the OM corresponds to anthracite to semi-graphite. OM maturation variation in the *Série Negra* succession is related to variable burial evolution and metamorphic/metasomatic processes in the Ossa-Morena Zone sectors. The sedimentary sources of the black shales are related to the break up of a Cadomian magmatic-arc developed in the North Gondwana realm, where the Ossa-Morena Zone was located during late Ediacaran times, showing acidic to mixed signatures. Some ratios were calculated based on redox sensitive elements, indicating both anoxic and oxic paleoenvironmental conditions. The anoxic conditions were predominant and they were identified on samples with higher

organic carbon content, emphasizing that the redox conditions favored OM preservation and the accumulation of selected metals. Considering the mode of occurrence, the elements Ag, Cd, Cu, Pb and Se are assumed to be preferentially associated with sulfides, whereas Mo and U are preferentially organically bound. The results reveal that the black shales from the *Série Negra* succession in Ossa-Morena Zone might represent a source of metals, which were probably remobilized during Variscan events.

2.1. Geological framework

The Iberian Massif is characterized by the presence of stratigraphic units from Neoproterozoic to Upper Paleozoic, that are divided in several tectonostratigraphic zones, among which the OMZ (e.g., Ribeiro et al., 2007; Dias et al., 2016). The OMZ is a heterogeneous and complex tectonostratigraphic zone, with unique stratigraphic, magmatic and tectono-metamorphic features, due to the presence of two successive Wilson Cycles, namely the Cadomian and Variscan Cycles (e.g., Oliveira et al., 1991; Eguíluz et al., 2000; Ribeiro et al., 2007, 2009; Moreira et al., 2014a; Quesada and Oliveira, 2019).

The Ediacaran record exposed in the OMZ commonly includes the *Série Negra* succession, initially described both in Portugal by Carvalhosa (1965) and in Spain by Alia (1963) and Vegas (1968). This metasedimentary succession outcrops in the core of NW-SE Variscan regional structures, namely: (1) the northern edge of the OMZ, outlined by Tomar-Badajoz-Córdoba Shear Zone (Blastomylonitic Belt) and the Obejo-Valsequillo-Puebla de la Reina Domain; (2) the core of the Estremoz, Olivenza-Monesterio and Vila Boim Anticlines located in Central Domains of OMZ; and (3) in the Almadén de la Plata-Aracena, Montemor-o-Novo, Moura, Viana do Alentejo and Serpa regions, in the OMZ Southern Domains (e.g., Apalategui et al., 1990; Quesada et al., 1990; Oliveira et al., 1991; Eguíluz et al., 2000; Pereira et al., 2006; 2012a; Araújo et al., 2013; Moreira et al., 2014b) (Fig. 1A). Two distinct metasedimentary units are included in the *Série Negra* Neoproterozoic succession of the Blastomylonitic Belt, from the bottom to the top (e.g., Oliveira et al., 1991; Eguíluz et al., 2000; Oliveira et al., 2003; Pereira et al., 2006):

- *Morenos* Formation: siliceous shales, black metacherts and quartzites, meta-arkoses and metapsammites and garnet-bearing micaschists, sometimes with interlayered felsic and mafic meta-volcanic rocks (similar to Montemolín succession described in Spain).

- *Mosteiros* Formation: includes a monotonous flysch sequence of black shales/schists, metagreywackes, black quartzites and metapsammites interlayered with black siliceous chemiogenic (metacherts/lydites; Pfefferkorn, 1968), presenting maximum deposition age around 540 Ma (e.g., Schäfer et al., 1993; Fernandez-Suarez et al., 2002; Linnemann et al., 2008; Pereira et al., 2012a). This unit is similar to Tentúdia succession in Spain.

Locally, the upper *Série Negra* succession presents different designations (Oliveira et al., 1991; Pereira et al., 2006): *Mosteiros* Formation in Blastomylonitic Belt and Alter do Chão - Elvas Sector, is considered equivalent of *Mares* Formation in Estremoz Anticline and *Águas de Peixe* Formation in Montemor - Ficalho Sector (Fig. 1).

The *Série Negra* succession has a distinct tectono-thermal evolution, depending on its location within the OMZ (Oliveira et al., 1991; Eguíluz et al., 2000; Pereira et al., 2006). Indeed, the Variscan metamorphic conditions are heterogeneous along the OMZ, being conditioned by first order tectonic structures (Moreira et al., 2014a). In the Blastomylonitic Belt and Montemor-o-Novo region, the *Mosteiros* Formation is highly deformed as a result of tectono-metamorphic episodes related to high strain sinistral shear zones during Devonian - Carboniferous times, imposing metamorphism from upper greenschist to amphibolite facies conditions (Chichorro et al., 2008; Pereira et al., 2012b). Otherwise, in the Alter do Chão - Elvas and in the Estremoz Anticline sectors, the metamorphic peak conditions are related to a regional low-grade greenschist facies metamorphism (Pereira et al., 2012a; Moreira et al., 2014b; 2019).

The existing data suggests that the OMZ Ediacaran succession is related to the evolution of the North peri-Gondwana terranes (e.g., Pereira et al., 2006; 2012a; Linnemann et al., 2008). During the Ediacaran, the sedimentary succession of this tectonostratigraphic zone records the inception of a magmatic arc and a corresponding back-arc basin. Hence, the sediments from the top of the *Série Negra* succession are interpreted as originating from the dismantling of this magmatic arc (López-Guijarro, 2006; Pereira et al., 2006; Linnemann et al., 2008; López-Guijarro et al., 2008; Sanchez-Lorda et al., 2014).

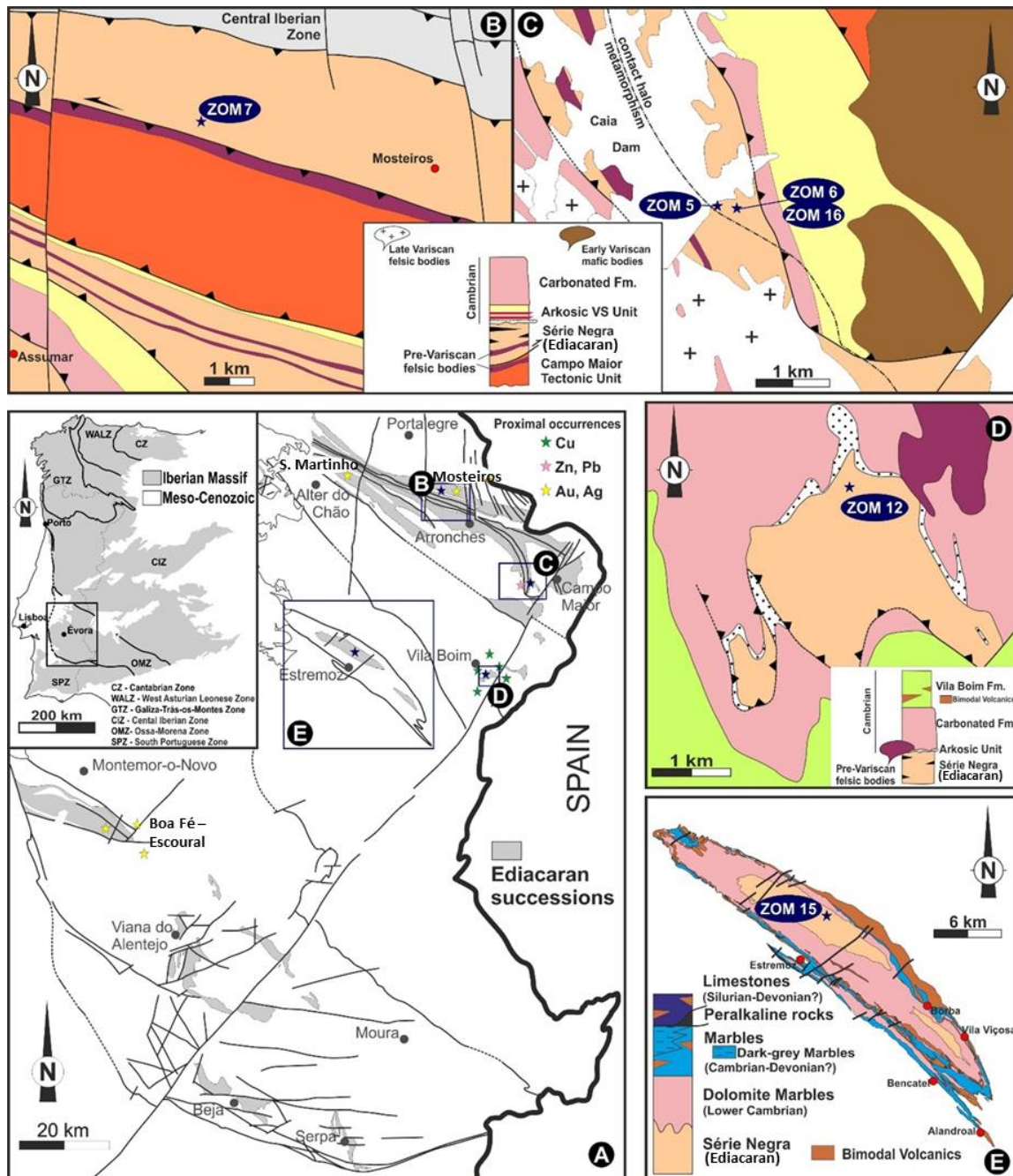


Figure 1 - Geological setting of the studied area and location of samples (adapted from Laranjeira et al., 2023; geological maps adapted from: A) LNEG, 2010; B) and C) LNEG, 2010; Pereira et al., 2010; 2012b; D) Moreira et al., 2014b; E) Moreira et al., 2019).

2.2. Sampling

Representative samples of low to medium-grade black shales from *Série Negra* succession outcropping in the different sectors from OMZ were collected. For sampling, the topmost layer has been removed to avoid the most weathered material. Visual inspection for mineralogical alteration allowed the removal of more altered parts of the samples. Samples ZOM 5, ZOM 6, ZOM 7, ZOM 16 were collected in the Blastomylonitic Belt (Fig. 1B, 1C), ZOM 12 was collected in the Alter do Chão - Elvas Sector (Fig. 1D), and sample ZOM 15 was collected in the Estremoz Anticline (Fig. 1E). Sample ZOM 16 (collected close to ZOM 6) was collected in the scope of a research project and the geochemical data was used in the present work.

Our data was complemented with previously published data, from other samples from the Ediacaran *Série Negra* succession of the OMZ (Pereira et al., 2006; Lopes, 2015; Lopes et al., 2015) namely the ones that were considered similar and, therefore, were used for comparison purposes. Two samples were described as very fine to fine-grained graphite-rich pelites (SN1 collected in Montemor-Ficalho sector and SN2 collected in the Blastomylonitic Belt, Fig. 1; Pereira et al., 2006). Four samples from Lopes (2015) were identified as metasedimentary lithologies containing graphite (LP1 to LP4 collected in Escoural - Montemor-o-Novo sector, Fig. 1). Pereira et al. (2006) reports that graphite-rich pelites are mainly composed of quartz, phyllosilicates and plagioclase with zircon, chlorite and apatite as accessory minerals. Laranjeira et al. (2023) also described the occurrence of iron oxides in addition to the previous mentioned detrital and metamorphic minerals. The applied methodologies are already explained in section 1.5.

2.3. Results

2.3.1. Organic matter characterization

The petrographic observations allowed the identification of organic particles in all samples. These particles are generally small, thin and elongated, occurring interbedded along with mineral matter. Figure 2 shows some petrographic features of the studied samples. In samples ZOM 5 and ZOM 6, organic particles are more abundant. In sample ZOM 5, the organic particles are larger and exhibit graphitic features (Fig 2). Graphitic structures were also observed in samples ZOM 7 and ZOM 12. The graphitic structures in samples ZOM 5, ZOM 7 and ZOM 12 occur principally as disseminated flakes associated with iron oxides (Fig. 2). The petrographic observation of sample ZOM 6

revealed small organic particles, sometimes with rounded shapes (Fig. 2), which can be acritarch remains. Acritarchs in the *Série Negra*, near the Caia dam (where samples ZOM 5 and ZOM 6 were collected), were previously described by Gonçalves and Palacios (1984).

The inorganic fraction is essentially composed of detrital derived minerals (mainly phyllosilicates and quartz), but the presence of iron oxides is common (Fig. 2). In samples ZOM 5 and ZOM 12, the presence of iron oxides is quite evident. This inorganic composition is consistent with results reported by other authors (Pereira et al., 2006; Chichorro et al., 2008).

The organic particles present R_r ranging from 2.41 % to 3.71 % and R_{max} varying between 4.13 % and 6.60 % (Table 1). Generally, samples from *Mosteiros* Fm. (ZOM 5, ZOM 6, ZOM 7 and ZOM 12) have higher OM reflectance ($R_r > 3\%$ and $R_{max} > 6\%$), demonstrating higher maturation than OM in a sample from *Mares* Fm. (ZOM 15) that has R_r and R_{max} of 2.41 % and 4.13 %, respectively. The R_{max} values indicate that the OM corresponds to anthracite ($R_{max} < 5\%$) in sample ZOM 15, and meta-anthracite in samples ZOM 5, ZOM 6, ZOM 7 and ZOM 12 ($5\% < R_{max} < 6.5\%$) (Kwiecinska and Petersen, 2004). Graphitization begins at a temperature of at least 300 °C and pressure (P), within the greenschist facies chlorite zone. It is completed before the amphibolite facies at temperatures from 380 to 450 °C (Kwiecinska and Petersen, 2004). Therefore, temperatures above 300 °C were expected in the studied *Série Negra* succession.

The TOC varies between 0.20% and 1.53% (Table 1). According to the classification of Huyck (1989) and Trabucho-Alexandre (2014), black shales contain TOC higher than 0.5%, which is noted for samples ZOM 6, ZOM 12 and ZOM 15. Despite these TOC values, OM's petrographic observation was more evident in samples ZOM 5 and ZOM 6, as can also be inferred based on the number of measured particles (N; Table 1). The S_t values are low, close to the detection limit in all samples (Table 1).

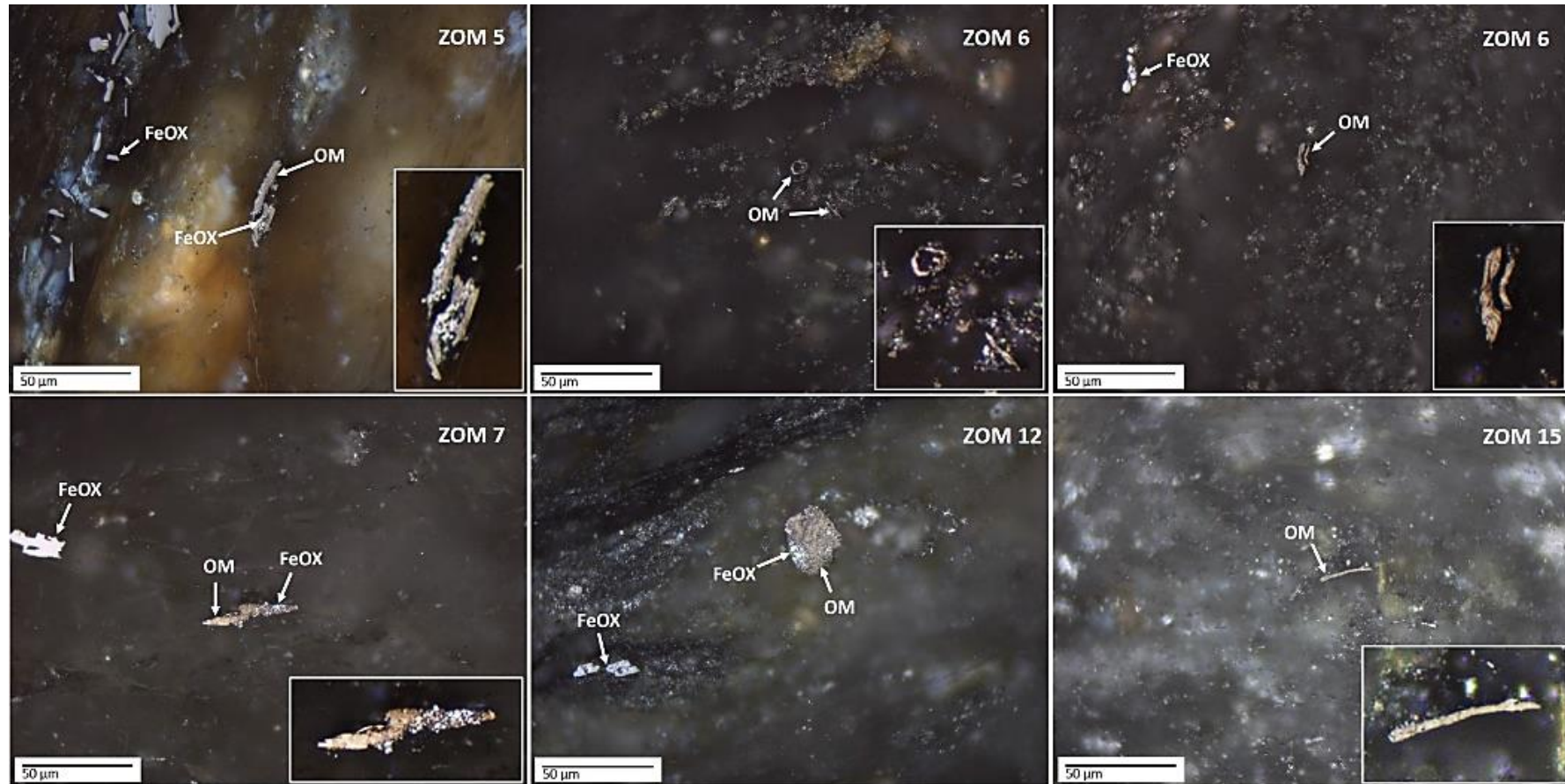


Figure 2 - Photomicrographs of the studied samples exhibiting organic particles occurring within mineral matter (OM - organic matter; FeOx - iron oxides). Photomicrographs taken in reflected white light and 50x immersion oil objective.

Table 1 - Random (R_r) and maximum reflectance (R_{max}) of organic particles, number of measured organic particles (N), standard deviation of random reflectance (SD), TOC and S_t contents.

	ZOM 5	ZOM 6	ZOM 7	ZOM 12	ZOM 15
R_r %	3.71	3.18	3.34	3.31	2.41
R_{max} %	6.60	5.17	5.19	5.37	4.13
N	21	21	7	6	4
SD	0.65	0.40	0.55	0.77	0.17
TOC %	0.20	1.53	0.29	1.08	0.76
S_t %	0.011	0.017	<0.010	<0.010	<0.010

2.3.2. Geochemical composition of black shales

Tables 2 and 3 present the geochemical composition of major, minor and trace elements of the studied samples, together with TOC and total sulfur (TS) (Laranjeira et al., 2023), as well as the composition of BBS, NASC, PAAS, AS and UCC for comparison.

The most abundant major and minor elements in the studied samples are Al, Fe, K and Na, followed by smaller amounts of Ca, Mg, P, S and Ti. The chemical composition is consistent with the mineralogical composition described for black shales derived lithotypes of the *Série Negra* (Pereira et al., 2006; Laranjeira et al., 2023).

Aluminum, Fe, K, and Na are the elements that have greater variability amongst the studied samples (Fig. 3). Generally, the samples show a similar pattern, except: (1) sample ZOM 6 that has distinct patterns for Fe, K and Mg content; and (2) sample ZOM 15 that has a worth noting higher K content.

Table 2 - Values of TOC (%), TS (%), concentration of major (wt. %), minor (wt. %) and trace elements (ppm) in the studied samples and reference values of BBS, NASC, PAAS, AS and UCC for comparison.

	Mosteiros Fm					Mares Fm	BBS ¹	NASC ²	PAAS ³	AS ⁴	UCC ⁵
	ZOM 5	ZOM 6	ZOM 7	ZOM 12	ZOM 16	ZOM 15					
TOC*	0.20	1.53	0.29	1.08	n.a	0.76	n.a	n.a	n.a	n.a	n.a
TS*	0.01	0.012	<0.01	<0.01	n.a	<0.01	n.a	n.a	n.a	n.a	n.a
Al	9.98	5.96	5.97	7.83	n.a	8.26	n.a	16.9	n.a	8.84	15.1
Ca	0.16	0.58	0.17	0.31	n.a	0.16	n.a	3.63	n.a	1.57	3.64
Fe	3.83	0.94	2.71	3.97	n.a	2.35	n.a	5.67	n.a	4.83	4.76
K	2.37	0.11	1.73	2.04	n.a	3.22	n.a	3.97	n.a	2.99	2.76
Mg	0.70	0.08	0.80	0.85	n.a	0.79	n.a	2.86	n.a	1.57	2.45
Na	0.27	2.55	2.12	1.48	n.a	0.93	n.a	1.14	n.a	1.19	3.55
P	0.05	0.03	0.06	0.06	n.a	0.01	0.93 - 2.20	0.13	n.a	0.07	0.17
Ti	0.54	0.16	0.33	0.49	n.a	0.47	1.50 - 4.60	0.70	n.a	0.47	0.56
Ag	0.01	0.40	0.05	0.03	0.25	0.05	0.40 - 2.40	0.01	0.05	0.07	0.05
As	7.90	18.4	14.6	13.4	9.00	53.3	10.0 - 80.0	n.a	1.50	10.0	4.80
Ba	769	146	521	636	676	1986	270 - 800	636	550	580	624
Be	3.00	2.00	2.00	3.00	n.a	2.00	1.00 - 3.00	n.a	3.00	3.00	2.10
Bi	<0.04	0.87	<0.04	0.47	n.a	0.14	0 - 4.00	0.01	0.13	0.13	0.16
Cd	<0.02	0.16	<0.02	<0.02	0.25	<0.02	2.00 - 12.0	0.03	0.10	0.13	0.09
Co	20.5	9.00	10.0	9.70	16.0	4.90	10.0 - 30.0	26.0	17.0	19.0	17.3
Cr	62.0	37.0	54.0	108	90.0	73.0	50.0 - 160	125	85.0	90.0	92.0
Cs	12.4	0.20	3.40	1.60	5.77	7.60	2.00 - 7.00	n.a	4.60	5.50	4.90
Cu	23.1	133	43.6	60.9	27.0	11.4	35.0 - 150	n.a	25.0	45.0	28.0
Ga	25.1	14.1	13.4	17.8	22.9	27.1	9.00 - 25.0	n.a	17.0	19.0	17.5
Hf	2.65	3.02	2.90	2.84	5.90	5.38	2.50 - 6.00	6.30	5.80	2.80	5.30
In	0.06	<0.01	0.04	0.06	n.a	0.08	n.a	n.a	0.05	n.a	0.06
Li	19.7	3.70	27.1	11.1	30.0	13.2	15.0 - 50.0	n.a	20.0	n.a	21.0
Mn	366	16.0	275	175	n.a	157	200 - 800	n.a	n.a	850	n.a
Mo	0.53	6.35	0.30	8.19	0.50	0.33	6.00 - 60.0	n.a	1.50	2.60	1.10
Nb	16.9	2.34	7.14	15.0	12.5	9.66	7.00 - 15.0	13.0	12.0	18.0	12.0
Ni	31.8	55.5	31.1	50.5	40.0	22.5	40.0 - 140	58.0	44.0	68.0	47.0
Pb	4.32	66.3	4.20	7.46	13.0	18.4	10.0 - 40.0	20.0	17.0	22.0	17.0
Rb	149	2.80	73.5	76.8	111	165	40.0 - 120	125	112	140	84.0
Sb	0.23	0.42	1.16	1.73	n.a	0.41	0.20 - 11.0	n.a	0.20	n.a	0.40
Sc	12.1	5.10	7.90	12.1	13.0	16.2	7.00 - 20.0	15.0	13.6	n.a	14.0
Se	<0.3	5.80	0.40	<0.3	n.a	0.40	3.00 - 30.0	0.08	0.05	0.60	0.09
Sn	3.70	0.60	1.70	2.30	3.00	11.5	2.00 - 10.0	n.a	5.50	n.a	2.10
Sr	45.0	202	96.0	68.0	138	85.0	100 - 300	142	350	300	320
Ta	1.30	0.20	0.50	1.10	1.00	0.80	0.50 - 1.00	1.10	1.00	2.00	0.90
Te	0.07	0.68	0.10	0.17	n.a	0.13	1.30 - 3.00	n.a	n.a	n.a	n.a
Tl	1.20	<0.05	0.42	0.34	5.00	0.75	0.50 - 10.0	n.a	n.a	0.68	0.90
Th	12.1	7.60	6.70	8.10	10.6	26.9	4.00 - 11.0	12.3	10.7	12.0	10.5
U	2.80	13.3	2.00	5.80	2.91	4.20	4.00 - 25.0	2.70	2.80	3.70	2.70
Y	11.7	22.6	5.50	18.5	27.5	19.1	15.0 - 40.0	35.0	22.0	41.0	21.0
V	97.0	147	84.0	284	105	110	100 - 400	130	107	130	97.0
W	3.20	1.10	1.20	1.80	3.00	3.50	0 - 15.0	n.a	2.00	n.a	1.90
Zn	40.9	35.1	82.5	33.3	100	33.8	60.0 - 300	n.a	71.0	95.0	67.0
Zr	80.5	112	97.5	99.4	207	163	60.0 - 190	200	190	160	193

¹Laranjeira et al., 2023; ²Ketris and Yudovich, 2009; ³Condie, 1993, Gromet et al., 1984, Taylor and McLennan, 1985; ⁴Taylor and McLennan, 1985, Condie, 1993; ⁵Wedepohl, 1971, Piper, 1974; ⁶Rudnick and Gao, 2014; n.a - data not available.

Table 3 - Concentration of REE (ppm) in the studied samples and reference values of BBS, NASC, PAAS, AS and UCC for comparison.

	Mosteiros Fm					Mares Fm	BBS ¹	NASC ²	PAAS ³	AS ⁴	UCC ⁵
	ZOM 5	ZOM 6	ZOM 7	ZOM 12	ZOM 16	ZOM 15					
La	31.5	40.1	24.3	31.2	40.1	80.5	20.0 - 40.0	31.1	38.0	41.0	31.0
Ce	92.4	83.9	51.4	63.0	76.6	145	35.0 - 80.0	66.7	80.0	83.0	63.0
Pr	8.40	9.90	6.40	8.20	9.34	17.6	2.50 - 6.00	7.70	8.83	10.1	7.10
Nd	30.5	37.4	21.6	32.0	33.5	58.3	15.0 - 45.0	27.4	32.0	38.0	27.0
Sm	5.40	7.50	4.30	6.10	6.64	9.70	2.50 - 7.00	5.59	5.60	7.50	4.70
Eu	1.20	1.70	0.90	1.70	1.21	2.90	1.00 - 1.40	1.18	1.10	1.61	1.00
Gd	5.20	6.10	3.30	4.40	5.15	6.50	2.50 - 6.00	4.90	4.70	6.35	4.00
Tb	0.70	0.70	0.40	0.70	0.82	0.70	0.50 - 0.90	0.85	0.77	1.23	0.70
Dy	3.40	4.30	1.40	4.40	5.19	3.90	1.00 - 4.00	4.17	4.68	5.50	3.90
Ho	0.50	0.70	0.20	0.70	0.97	0.50	0.20 - 0.60	1.02	0.99	1.34	0.83
Er	1.30	1.90	0.80	1.90	2.90	1.70	1.00 - 2.00	2.84	2.85	3.75	2.30
Tm	0.20	0.30	0.10	0.30	0.39	0.40	0.30 - 0.55	0.84	0.40	0.63	0.30
Yb	1.20	1.90	0.90	2.10	2.86	2.20	2.00 - 3.50	3.06	2.80	3.53	2.00
Lu	0.20	0.30	0.20	0.30	0.41	0.40	0.30 - 0.45	0.46	0.43	0.61	0.31
ΣLREE	168	178	107	140	166	311	75.0 - 178	139	164	180	133
ΣHREE	13.9	17.9	8.20	16.5	19.9	19.2	8.80 - 19.4	19.3	18.7	24.6	15.3
ΣREE	182	196	115	157	186	330	83.8 - 197	158	183	204	148
Ce/Ce*	1.30	0.96	0.94	0.90	0.91	0.88	n.a	n.a	n.a	n.a	n.a
Eu/Eu*	1.05	1.17	1.11	1.53	0.96	1.69	n.a	n.a	n.a	n.a	n.a

¹Ketris and Yudovich, 2009; ²Condie, 1993, Gromet et al., 1984, Taylor and McLennan, 1985; ³Taylor and McLennan, 1985, Condie, 1993; ⁴Wedepohl, 1971; Phipps, 1974; ⁵Rudnick and Gao, 2014; Ce/Ce* Bau and Dulski, 1996; Eu/Eu* Taylor and McLennan, 1985; LREE - light rare earth elements; HREE - heavy rare earth elements; n.a - data not available.

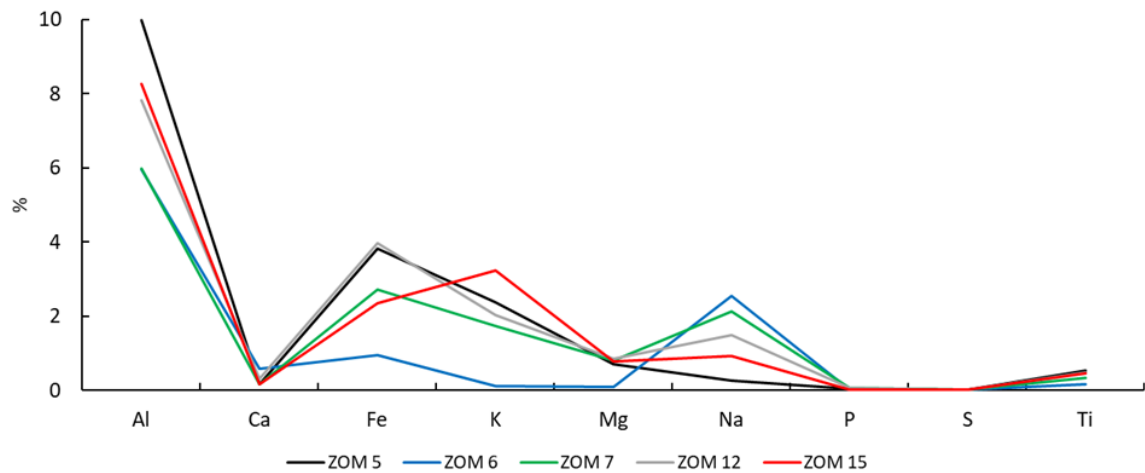


Figure 3 - Concentration of major and minor elements (wt. %) in the studied samples.

The concentration and distribution pattern of selected trace elements is illustrated in Figure 4. Generally, the elements As, Ba, Be, Co, Cr, Cu, Ga, Hf, Mn, Nb, Ni, Pb, Rb, Sc, Sr, Th, U, Y, V, W, Zn and Zr are found in concentrations above 1 ppm. Elements with concentrations below 1 ppm are Ag, Bi, Cd, In, Ta, Te and Tl. The elements Cs, Mo, Sb, Se and Sn are found in concentrations above and below 1 ppm.

The distribution pattern of the selected elements is quite similar, except for the samples ZOM 6 and ZOM 15. These differences are particularly evident for ZOM 6 sample with lower concentrations of Ba, Cs, In, Li, Mn, Nb, Rb, and Tl content; whereas the elements Ag, Cd, Cu, Pb, Se, Te and U display higher concentrations (Fig. 4, Tables 2 and 3). Sample ZOM 15 also stands out due to the higher concentrations of As, Ba, Th and Σ LREE (Fig. 4, Tables 2 and 3).

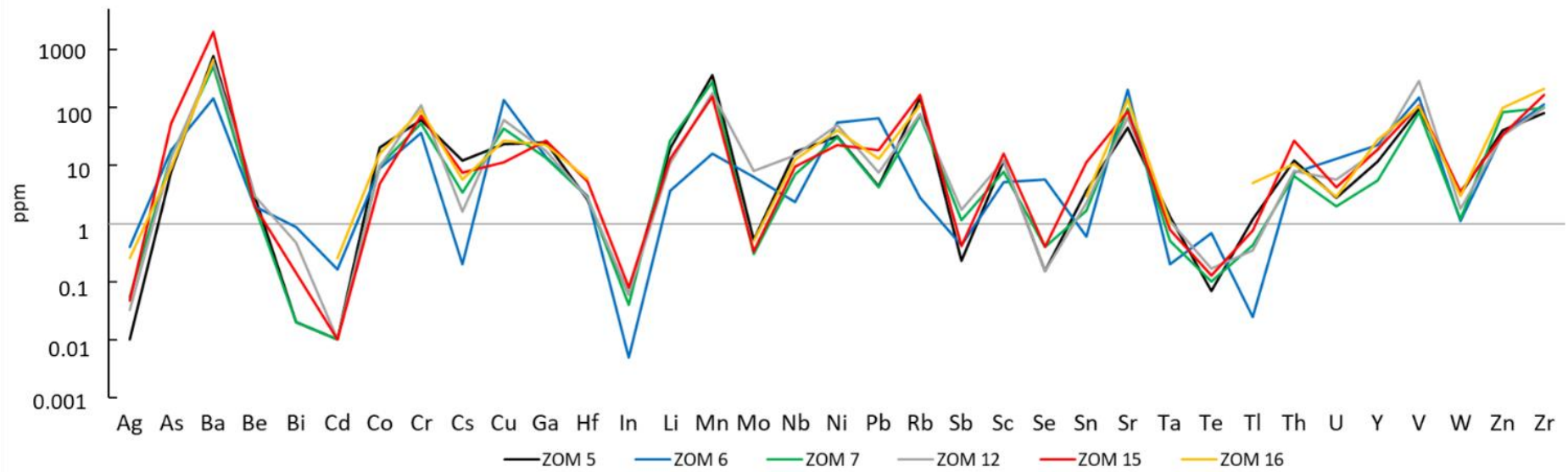


Figure 4 - Concentration of trace elements (ppm) in the studied samples.

The Σ REE varies from 115 ppm to 330 ppm, with an average value of 194 ppm (Table 3). The REE patterns of the studied samples normalized to BBS (maximum), NASC, PAAS and AS are presented in Figure 5. The normalized patterns are relatively similar, showing flattened profiles, that are successively less smooth and depleted in heavy REE (HREE) (Fig. 5). This depletion is common in black shales, demonstrating that the patterns were not severely affected by the diagenesis, weathering and metamorphism of the rocks (Boyong et al., 2011). Sample ZOM 7 shows evidence for more differentiated and depleted profiles than the other samples, principally for HREE. Sample ZOM 15 exhibits a more differentiated and enriched profile for light REE (LREE).

In order to compare the geochemical composition of samples with reference values, specifically the BBS (Ketris and Yudovich, 2009), NASC (Gromet et al., 1984; Taylor and McLennan, 1985; Condie, 1993), PAAS (Taylor and McLennan, 1985; Condie, 1993), AS (Wedepohl, 1971; Piper, 1974) and UCC (Rudnick and Gao, 2014), concentration coefficients (CC) were calculated.

The ratio between elements concentration in the samples and their concentration in reference data gives information about the enrichment ($CC > 1$) or depletion ($CC < 1$) of those elements in the studied black shales comparatively to the reference materials. Considering the range for BBS, the CC were calculated considering the maximum values. For REE, the CC were calculated considering the sum of LREE and HREE. Table 4 displays, for each sample, the group of elements having $1 < CC < 2$, $2 < CC < 10$, and $CC > 10$, indicating an increasing degree of enrichment.

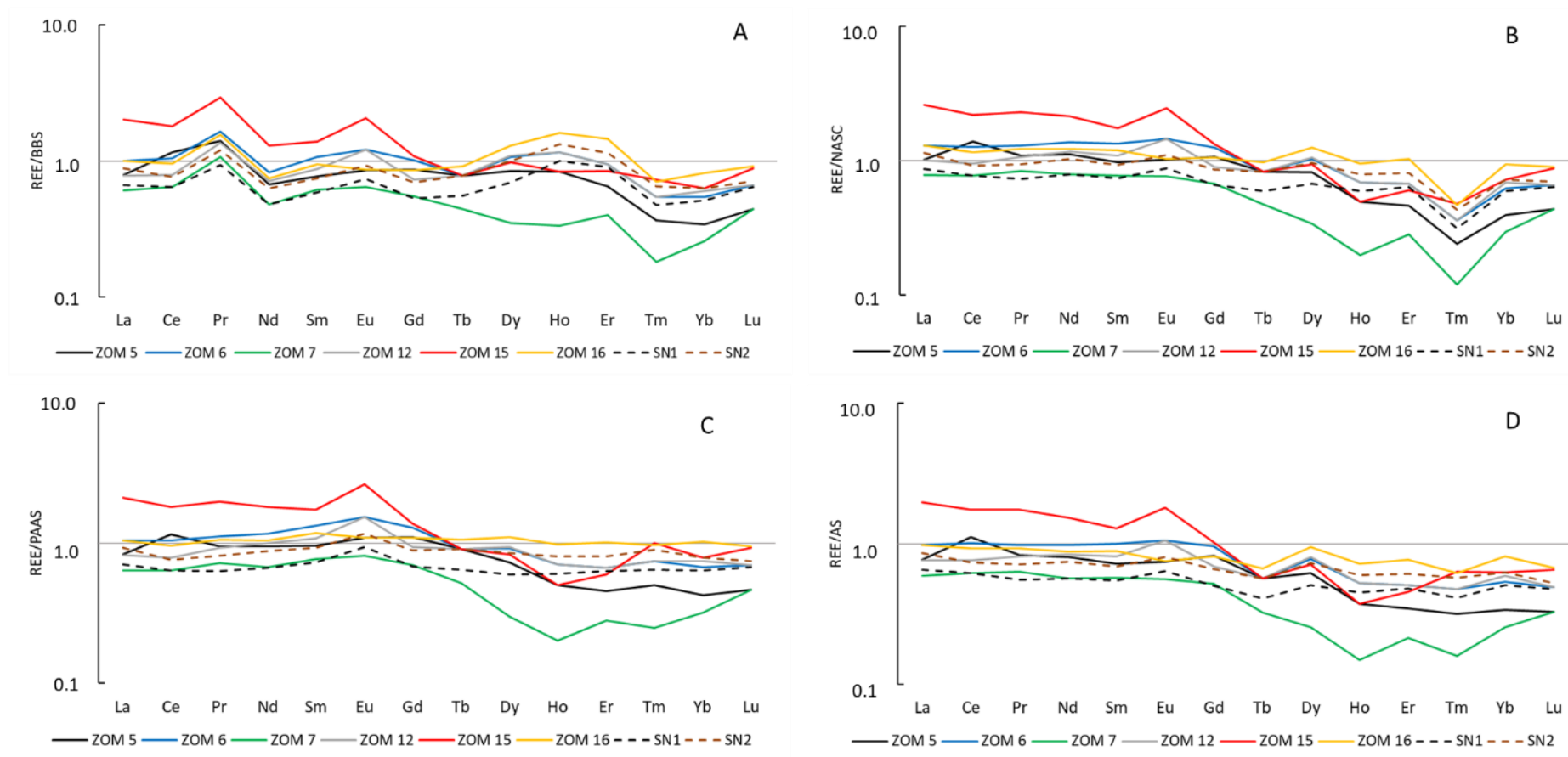


Figure 5 - REE patterns for the studied samples and from graphite-rich pelites from *Série Negra* of OMZ (SN1 and SN2): A) BBS-normalized REE patterns; B) NASC-normalized REE patterns; C) PAAS-normalized REE patterns; and D) AS-normalized REE patterns.

Table 4 - Concentration coefficients (CC) of trace elements in the studied samples relatively to BBS, NASC, PAAS, AS and UCC.

Samples	1 < CC < 2	2 < CC < 10	CC > 10
BBS	ZOM 5	Cs, Nb, Rb, Ta, Th	
	ZOM 6	Pb	
	ZOM 7		
	ZOM 12	Ta	
	ZOM 15	Cs, Ga, Rb, Sn, LREE	Ba, Th
	ZOM 16	Zr, HREE	
NASC	ZOM 5	Ba, Nb, Rb, Se, Ta, U, LREE	Bi
	ZOM 6	Sr, V, LREE	Cd, Pb, U
	ZOM 7		Ag, Bi, Se
	ZOM 12	Nb, Se, LREE	Ag, U, V
	ZOM 15	Rb, Sc, U	Ag, Ba, Se, Th, LREE
	ZOM 16	Ba, U, Zr, LREE, HREE	Cd
PAAS	ZOM 5	Ba, Co, Ga, In, Nb, Rb, Sb, Ta, Th, W, LREE	As, Cs, Se
	ZOM 6	Cd, Ni, Y, V, LREE, HREE	Ag, Bi, Cu, Mo, Pb, Sb, U
	ZOM 7	Ag, Cu, Li, Zn	As, Sb, Se
	ZOM 12	Ba, Cr, Ga, In, Nb, Ni, Ta, LREE, HREE	As, Bi, Cu, Mo, Sb, Se, U, V
	ZOM 15	Bi, Cs, Ga, In, Pb, Rb, Sc, U, V, W, HREE	Ba, Sb, Se, Sn, Th, LREE
	ZOM 16	Ba, Cr, Cs, Cu, Ga, Hf, Li, Nb, U, Y, W, Zn, Zr, LREE, HREE	Ag, As, Cd
AS	ZOM 5	Ba, Co, Ga, Rb, Tl, Th	Cs
	ZOM 6	As, Cd, Hf, V	Ag, Bi, Cu, Mo, Pb, Se, U
	ZOM 7	As, Hf	
	ZOM 12	As, Ba, Cr, Cu, Hf, U	Bi, Mo, V
	ZOM 15	Bi, Cs, Ga, Hf, Rb, Tl, U, Zr, LREE	As, Ba, Th
	ZOM 16	Ba, Cd, Cs, Ga, Zn, Zr	Ag, Hf, Tl
UCC	ZOM 5	As, Ba, Be, Co, Ga, In, Nb, Rb, Se, Sn, Ta, Tl, U, W, LREE	Cs
	ZOM 6	Cd, Ni, Sb, Y, V, LREE, HREE	Ag, As, Bi, Cu, Mo, Pb, U
	ZOM 7	Ag, Cu, Li, Zn	As, Sb, Se
	ZOM 12	Ba, Be, Cr, Ga, In, Nb, Ni, Se, Sn, Ta, LREE, HREE	As, Bi, Cu, Mo, Sb, U, V
	ZOM 15	Cs, Ga, Hf, In, Pb, Rb, Sb, Sc, U, V, W, HREE	Ba, Se, Sn, Th, LREE
	ZOM 16	As, Ba, Cs, Ga, Hf, Li, Nb, Rb, Sn, Ta, Th, U, Y, V, W, Zn, Zr, LREE, HREE	Ag, Cd, Tl

The determination of CC reveals that many elements are depleted or have concentration similar to those from the reference materials, being normal ($CC < 1$) to slightly enriched ($1 < CC < 2$) (Table 4). Considering the BBS, only Ba and Th are enriched in sample ZOM 15. For the other reference materials, this is, for NASC, PAAS, AS and UCC, some elements (Ag, As, Cs, Ba, Bi, Cd, Cu, Mo, Pb, Sb, Sn, Se, Th, Tl, U, V, and LREE) generally have $CC > 2$, although Ag, As, Bi, and Se have $CC > 10$ in some samples (mostly ZOM 6 and ZOM 15; Table 4). The elements showing $CC > 10$ are chalcophile elements, with low affinity for oxygen and preferentially bonded with sulfur to form sulfides.

Samples ZOM 6, ZOM 12, and ZOM 15 stand out by their greater number of elements with $CC > 2$ considering all the reference materials, being the majority chalcophile elements. In sample ZOM 6, elements with $CC > 2$ are: Ag, As, Bi, Cd, Cu, Mo, Sb, Se, Pb, and U; the enrichment in Pb was only noticed in this sample. In sample ZOM 12, elements with $CC > 2$ are: As, Bi, Cu, Mo, Sb, Se, U, and V. In sample ZOM 15, the only sample from the Mares Fm., elements with $CC > 2$ are: As, Ba, Bi, Sb, Se, Sn, Th, and LREE; the enrichment in Th and LREE was only noticed in this sample. It must be remarked that the samples that contain the most significant enrichment of trace elements correspond to the samples that have greater TOC content (Table 2).

2.3.3. Microscopic analysis

The SEM-EDX analyses of the black shales support and provide new insights about their geochemical composition, elemental distribution, and mineralogical content. The SEM-EDX analysis was performed in selected samples (ZOM 6 and ZOM 15). The analyses allow the identification of aluminosilicates, Fe and Ti oxides, and OM in both samples (Figs. 5 and 6). The identified minerals corroborate the previous petrographic observations (Laranjeira et al., 2023).

In the sample ZOM 6, the SEM analysis shows abundant aluminosilicates (Fig. 6, spectrum Z1), including some particles occurring in association with Fe oxides (Fig. 6, spectrum Z3) and with Ti oxides (Fig. 6, spectrum Z2); the detection of inorganic elements from both the aluminosilicates and Fe and Ti oxides in spectra (Fig. 6, spectra Z2 and Z3) evidence their association.

In sample ZOM 15, it was also possible to observe the occurrence of aluminosilicates (Fig. 7A, spectra Z1 and Z3) in association with Fe, Mn and Ti oxides (Fig. 7A, spectrum Z2) and with sulfides, namely arsenopyrite and pyrite (Fig. 7A, respectively spectra Z4

and Z5). The observation of Ti oxides in both samples and the significant positive correlation between Fe, Mn and Ti (Table 5) may indicate the presence of ilmenite.

In Figure 7B it is possible to observe the occurrence of particles exhibiting the association of Fe oxides (Fig. 7B, spectrum Z7) with OM (Fig. 7B, spectrum Z6) within aluminosilicates (Fig. 7B, spectrum Z8). This is supported by the positive correlation coefficients between TOC and some elements preferentially associated with sulfides. The detection of inorganic elements besides C in spectrum Z6 is related to its occurrence within mineral matter.

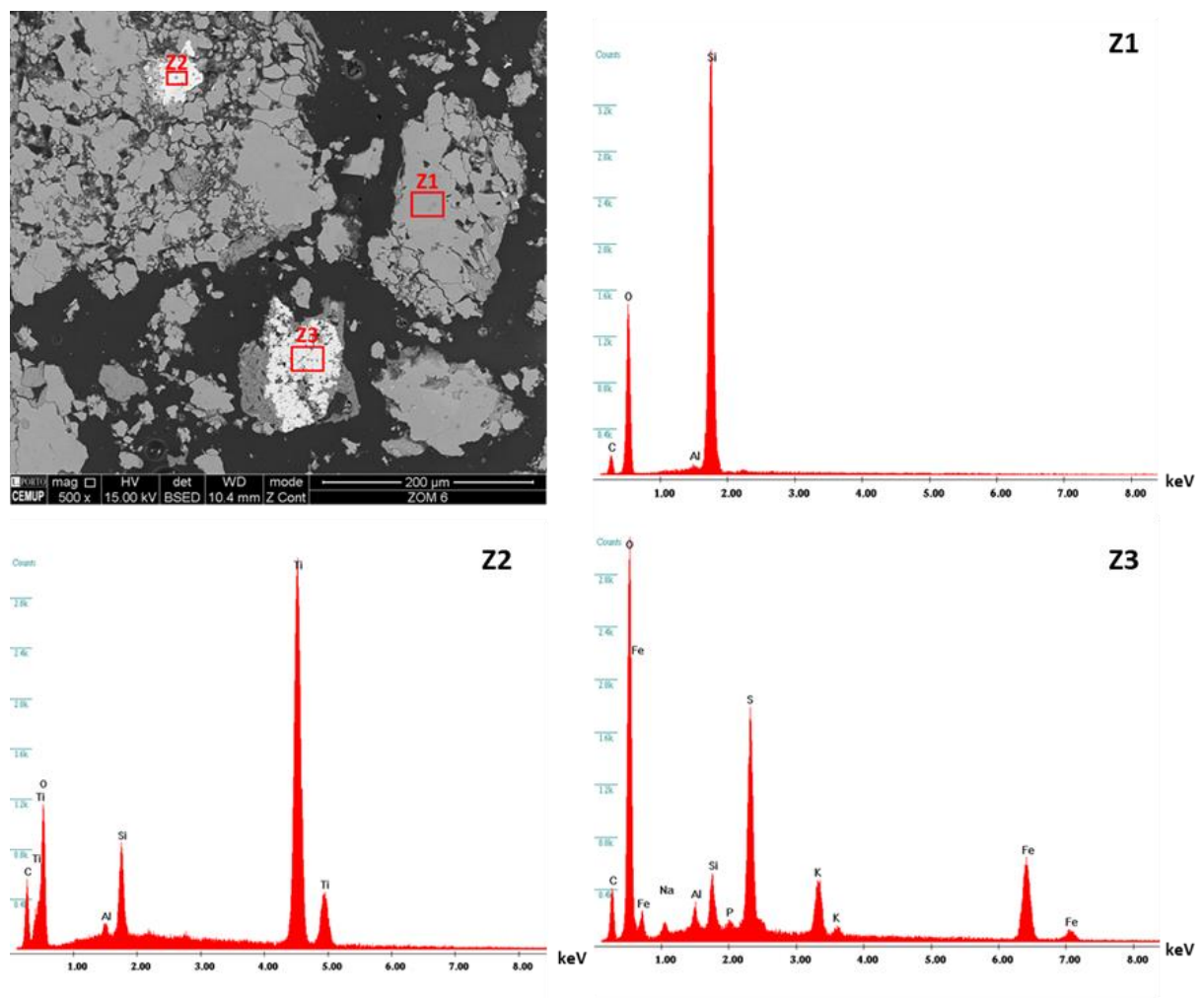


Figure 6 - SEM image and EDX spectra of aluminosilicates (Z1), titanium oxides and associated aluminosilicates (Z2), and iron oxides and associated mineral matter (Z3) in sample ZOM 6.

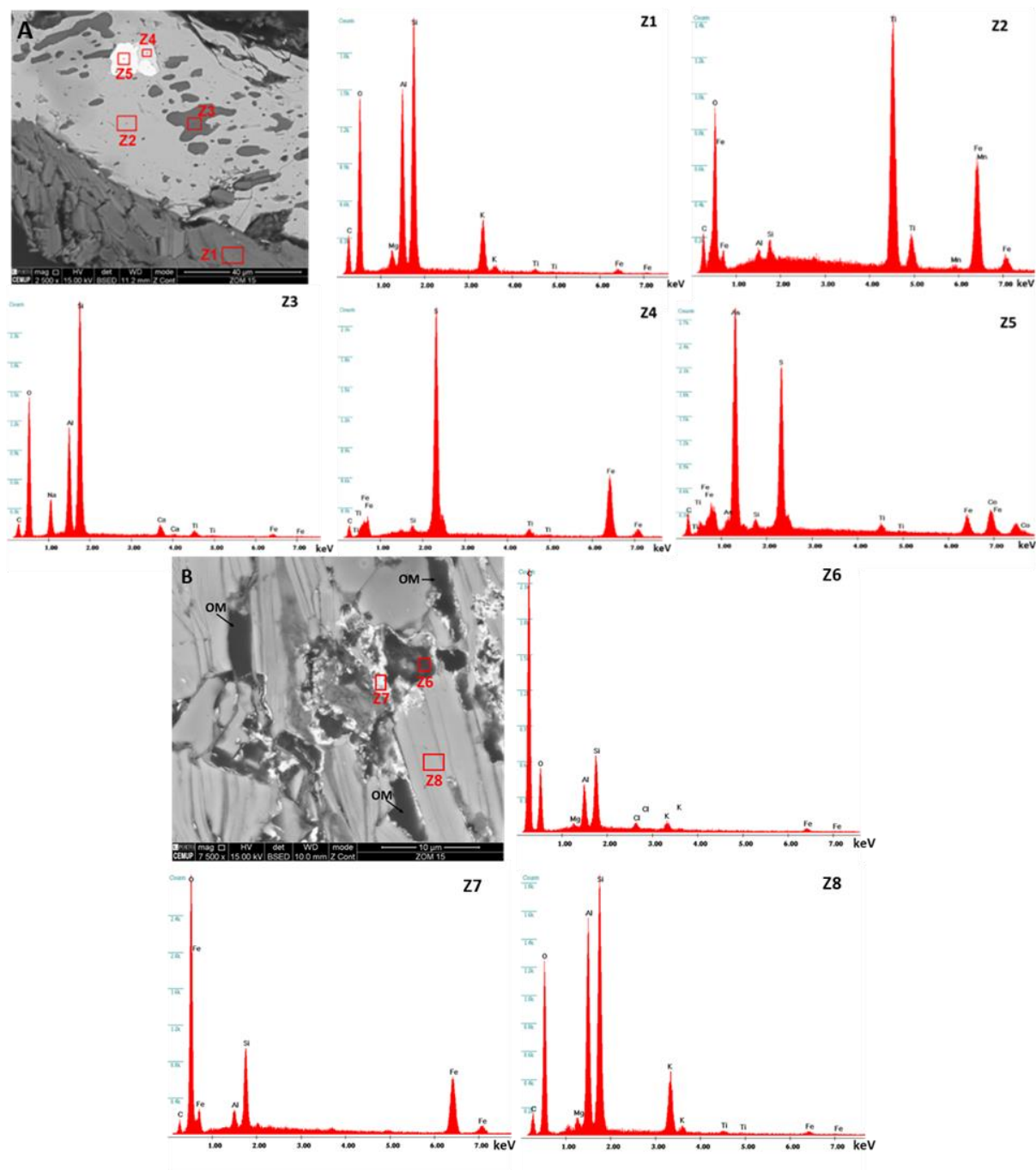


Figure 7 - SEM images and EDX spectra of: A) aluminosilicates (Z1 and Z3) and associated mineral matter, titanium oxide (Z2), pyrite (Z4) and arsenopyrite (Z5) in sample ZOM 15; B) organic matter and associated mineral matter (principally aluminosilicates) (Z6), iron oxides and associated aluminosilicates (Z7) and aluminosilicates (Z8) in sample ZOM 15.

2.4. Discussion

The OM maturation in *Mosteiros* Formation (ZOM 5, ZOM 6 and ZOM 7), included in the Blastomylonite belt, together with data from the literature, can be interpreted as related to the Early Carboniferous metamorphic event during Variscan Cycle (Pereira et al. 2012a), which according to Pereira et al. (2010), can reach temperatures higher than 500° C in the Blastomylonite belt. The higher R_{max} in samples ZOM 5 and ZOM 12 can be associated to the proximity to plutonic bodies (Figs. 1C, 1D) and to the metasomatic fluid percolation evidenced by the greater amounts of iron oxides, and also recognized in the *Série Negra* succession near the location of sample ZOM 5 (Cruz, 2013). The maturation observed in sample ZOM 15 should represent the effect of the regional Variscan metamorphism in greenschists facies (ca. 300-400° C; Pereira et al. 2012b, Moreira et al. 2019).

2.4.1. Elemental distribution

The Pearson correlation coefficients were calculated, and particular attention was given to the enriched elements ($CC > 2$). Table 5 shows the Pearson's correlation coefficients for selected elements.

Table 5 - Pearson correlation coefficients of selected elements. Strong positive correlations (> 0.75) are identified in blue, and strong negative correlations are marked in red (> -0.75).

	TOC	S	Al	Fe	Ti	Ag	As	Bi	Cd	Cu	Mn	Mo	Ni	Pb	Sb	Se	Te	U	Y	V
TOC																				
S	0.48																			
Al	-0.47	-0.15																		
Fe	-0.58	-0.58	0.67																	
Ti	-0.61	-0.61	0.87	0.88																
Ag	0.77	0.83	-0.61	-0.87	-0.91															
As	0.15	-0.31	0.03	-0.35	0.07	-0.04														
Bi	0.96	0.65	-0.49	-0.58	-0.69	0.86	-0.09													
Cd	0.76	0.88	-0.54	-0.82	-0.87	0.99	-0.10	0.86												
Cu	0.80	0.74	-0.66	-0.64	-0.85	0.92	-0.33	0.92	0.92											
Mn	-0.95	-0.41	0.60	0.76	0.71	-0.81	-0.35	-0.88	-0.77	-0.74										
Mo	0.81	0.28	-0.29	-0.07	-0.31	0.45	-0.31	0.83	0.47	0.71	-0.62									
Ni	0.78	0.56	-0.42	-0.24	-0.54	0.66	-0.51	0.89	0.69	0.89	-0.60	0.92								
Pb	0.82	0.81	-0.51	-0.88	-0.83	0.98	0.12	0.86	0.98	0.85	-0.85	0.43	0.60							
Sb	0.11	-0.57	-0.32	0.43	0.10	-0.29	-0.29	0.07	-0.33	0.06	-0.01	0.52	0.34	-0.38						
Se	0.76	0.86	-0.57	-0.85	-0.88	1.00	-0.06	0.85	1.00	0.91	-0.78	0.44	0.66	0.98	-0.33					
Te	0.85	0.81	-0.57	-0.81	-0.86	0.99	-0.06	0.92	0.99	0.94	-0.85	0.57	0.74	0.98	-0.22	0.99				
U	0.92	0.77	-0.47	-0.72	-0.75	0.94	-0.02	0.97	0.95	0.91	-0.88	0.68	0.79	0.95	-0.16	0.94	0.98			
Y	0.87	0.43	-0.03	-0.42	-0.26	0.57	0.38	0.78	0.58	0.50	-0.81	0.63	0.52	0.70	-0.16	0.57	0.66	0.78		
V	0.56	-0.14	-0.02	0.32	0.12	0.00	-0.20	0.51	0.02	0.30	-0.35	0.89	0.66	0.01	0.71	-0.01	0.14	0.30	0.49	

The results reveal a significant positive correlation coefficient between TOC and the trace elements Ag, Bi, Cd, Cu, Mo, Ni, Pb, Se, Sr, Te, U, and Y ($r > 0.75$; Table 5). The association of some of these elements with OM has been already reported in the literature (e.g. Ross and Bustin, 2009; El-Anwar et al., 2018; Finkelman et al., 2018; Ribeiro et al., 2019). However, the preferential affinity of some of them with sulfides is also noticeable. To investigate the sulfides affinity, the correlation coefficients with S was analyzed; it was found a weak positive correlation with TOC ($r = 0.48$) and a strong positive correlation ($r > 0.75$) with elements normally present in sulfides (Ag, Cd, Cu, Pb, and Se) (El-Anwar et al., 2018; Finkelman et al., 2018). Therefore, Ag, Cd, Cu, Pb and Se are thought to be preferentially associated with sulfides, whereas the elements Mo and U might be preferentially organically bound.

The moderate positive correlation between TOC and S indicates the occurrence of sulfides in association with OM, which corroborates the previous petrographic characterization of these samples (Laranjeira et al., 2023). The petrography revealed the occurrence of OM associated with iron oxides, including oxidized pyrite, and other sulfides. Iron displays positive correlation with Al, Ti and Mn, which indicates its association with aluminosilicates and oxides. In addition, for the referred elements, Ag, Bi, Cd, Cu, Mo, Pb, and Se they present $CC > 2$ in the studied black shales comparatively to reference materials (except BBS), reinforcing their importance in the studied samples, and the importance of the occurrence of OM in association with sulfides and oxides.

Most of the other elements have a negative correlation with TOC and a positive correlation with Al, pointing out their association with aluminosilicates (El-Anwar et al., 2018; Finkelman et al., 2018). These include, among others, Ba, Sn, Th, Tl, and LREE, which also have $CC > 2$.

2.4.2. Sedimentary sources and geochemical proxies of paleo-redox environments

The geochemical discriminant diagrams (Bhatia and Crook, 1986; Floyd and Leveridge, 1987) show that the clastic compounds of black shales derived essentially from a Continental Island Arc source (Figs. 8A and 8B), with acidic to mixed felsic/basic signatures (Fig. 8C). This data is consistent with the one obtained in previous works for diverse lithotypes including metamorphosed greywackes and shales, as well as para-derived high temperature lithotypes from *Série Negra* succession (Lopez-Guijarro, 2006; Pereira et al., 2006; Lopes, 2015; Lopes et al., 2015). This data is also in accordance with the main geodynamic model proposed for the evolution of OMZ, which indicates the

development of magmatic-arc and related back-arc basin in the North Gondwana realm, where the OMZ was located, during late Ediacaran times (e.g. Pereira et al., 2006; Chichorro et al., 2008; Linnemann et al., 2008; Sanchez-Lórda et al., 2014).

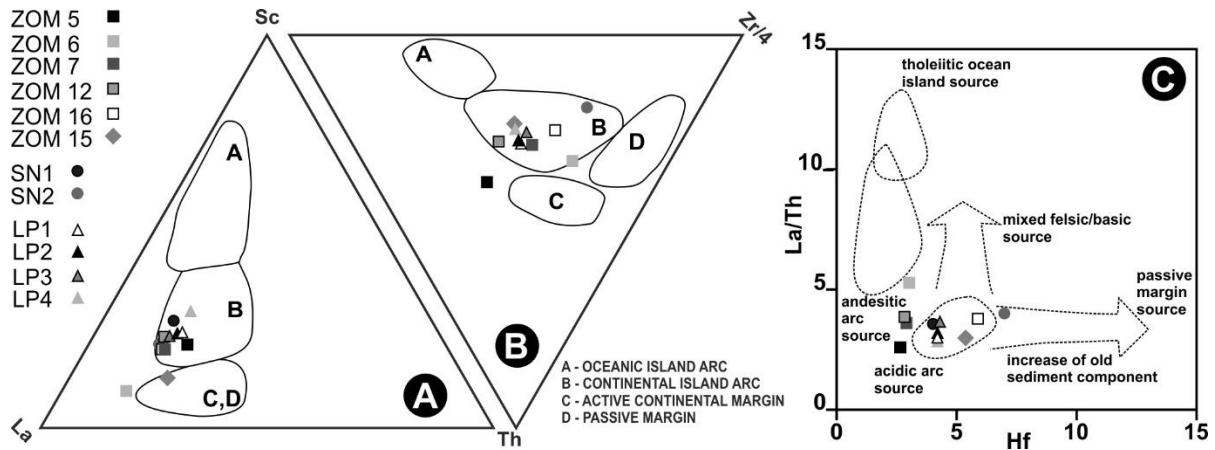


Figure 8 - A) Ternary La-Th-Sc diagram adapted from Bhatia and Crook (1986); B) Ternary Th-Sc-Zr/4 diagram adapted from Bhatia and Crook (1986) and C) La/Th-Hf diagram from Floyd and Leveridge (1987).

The ratio between some trace elements (e.g. Co, Cr, Cu, Mo, Ni, Th, U, V, Zn) has also been used as proxies for evaluation of redox depositional conditions during the sedimentary processes (e.g. Jones and Manning, 1994; Arning et al., 2009; Pi et al., 2013; El-Anwar et al., 2018; Ferreira et al., 2020). The ratios V/Cr, Ni/Co, U/Th and (Cu+Mo)/Zn, whose values increase under anoxic conditions, were calculated. Complementarily, TOC/Al and U/Mo for the studied samples were also determined and are all presented in Table 6.

Table 6 - Ratio of selected redox sensitive elements for the studied samples.

	ZOM 5	ZOM 6	ZOM 7	ZOM 12	ZOM 15	ZOM 16
V/Cr	1.56	3.97	1.56	2.63	1.51	1.17
Ni/Co	1.55	6.17	3.11	5.21	4.59	2.50
U/Th	0.23	1.75	0.30	0.72	0.16	0.27
U/Mo	5.28	2.09	6.67	0.71	12.7	5.82
(Cu+Mo)/Zn	0.58	3.97	0.53	2.07	0.35	0.28
TOC/Al	0.02	0.26	0.05	0.14	0.09	-

The ratio V/Cr in samples ZOM 6 (3.97) and ZOM 12 (2.63) indicate anoxic conditions, while the other values, ranging from 1.17 to 1.56, point to more oxidizing conditions (according to Jones and Manning, 1994, values of the ratio V/Cr above 2 indicate anoxic depositional conditions). Samples ZOM 6 and ZOM 12 present the higher V concentrations (147 ppm and 284 ppm, respectively), which indicate a V enrichment in these samples compared with reference materials (except the maximum for BBS) and supports the fact that V is more concentrated in sediments deposited under reducing conditions (e.g., Shaw et al., 1990; Emerson and Huested, 1991; Jones and Manning, 1994).

Similar paleo-redox conditions are also emphasized by the ratio (Cu+Mo)/Zn, indicator of the oxygenation of bottom waters (Hallberg 1976, 1982), which show higher ratio values in samples ZOM 6 (3.97) and ZOM 12 (2.07).

The high values of Ni/Co ratio show similar behavior for samples ZOM 6 and ZOM 12, including the sample ZOM 15 (Table 6) on samples that emphasize stronger reducing conditions during depositional processes (e.g., Dypvik, 1984; Dill, 1986; Jones and Manning, 1994). Tribovillard et al. (2006) suggested that the presence of Ni can be used as a proxy for primary paleoproductivity due to its accumulation in organic-rich sediments, which is also in accordance with the CC between TOC and Ni (Table 5).

The ratio U/Th is also usually used as a redox indicator (e.g., Adams and Weaver, 1958; Roger and Adams, 1969 in Jones and Manning, 1994; Ferreira et al., 2020). The increase of U/Th ratio is expected with the increase of anoxic conditions due to the accumulation of authigenic U in organic sediments, that is enhanced during deposition under progressively greater oxygen depletion (Ferreira et al., 2020). Indeed, the projection of U/Th and V/Cr ratios (Fig. 9) reveals that sample ZOM 6 is associated with anoxic conditions (similar to BBS) and sample ZOM 12 is associated with a suboxic domain. The other samples and reference materials are projected in the oxic conditions field, as well as organic-rich pelites of Pereira et al. (2006) and metasedimentary lithologies with graphite from Lopes (2015).

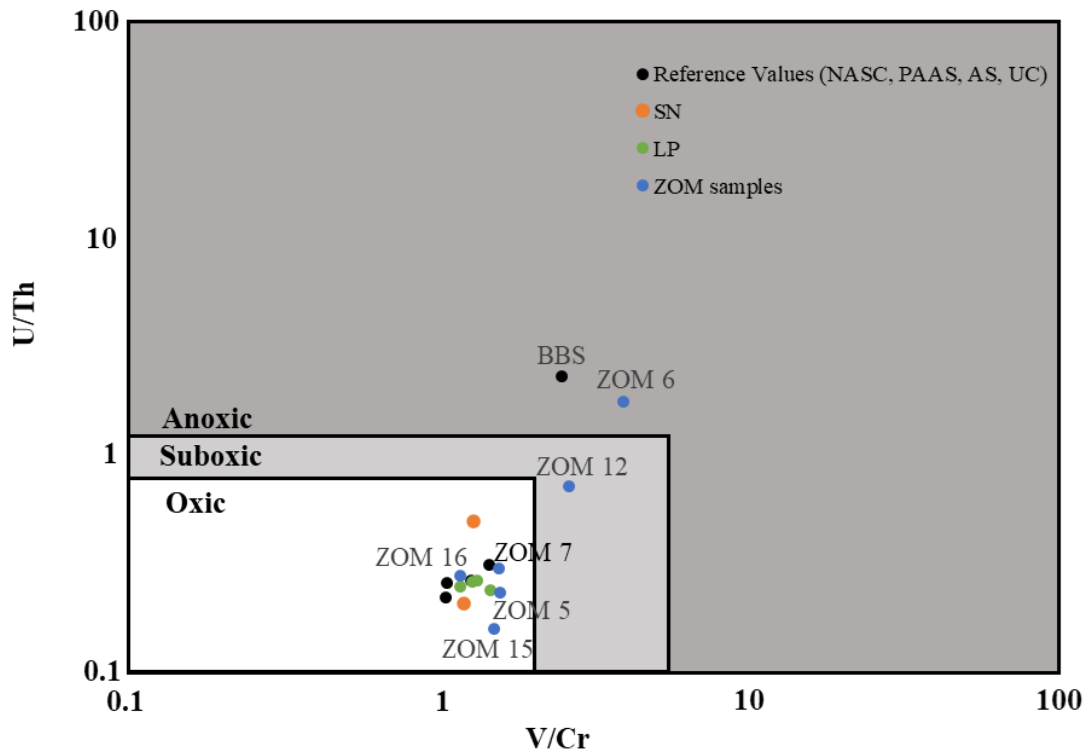


Figure 9 - Cross plot of redox-sensitive trace elements ratios (U/Th versus V/Cr; adapted from Piercey et al., 2016) of the studied samples and reference materials for comparison. SN - samples from Pereira et al. (2006); LP - samples from Lopes (2015); BBS (Ketris and Yudovich, 2009); NASC (Gromet et al., 1984; Taylor and McLennan, 1985; Condie, 1993); PAAS (Taylor and McLennan, 1985, Condie, 1993); AS (Wedepohl, 1971; Piper, 1974) and UCC (Rudnick and Gao, 2014).

The ratio U/Mo has also been used to differentiate between anoxic non-sulfidic and anoxic sulfidic conditions (Arning et al., 2009). The lowest values of U/Mo were obtained for samples ZOM 6 (2.09) and ZOM 12 (0.71), resulting from highest Mo concentration in this samples and, therefore, indicating that were deposited under more anoxic sulfidic conditions (Algeo et al., 2004; 2006). This is also supported by the higher concentration of elements with affinity with sulfides on sample ZOM 6.

The Eu and Ce anomalies are also important proxies because these elements are sensitive to changes in redox conditions due to their different behaviour when compared to other REE (Leybourne et al., 2000):

- The normalized patterns reveal a positive Eu anomaly for almost all samples ($\text{Eu}/\text{Eu}^* = 0.96\text{-}1.69$, average 1.25; Table 3; Fig. 5). The higher Eu positive anomalies in samples ZOM 6, ZOM 12 and ZOM 15 could be related either with the presence of detrital plagioclase and/or the anoxic conditions during depositional processes.

- The Ce negative anomaly was identified as a consequence of the change in the oxidation state of Ce (Elderfield and Greaves, 1982) and can also be used as an indicator of intensity of anoxia depending on the depositional setting (e.g., Murray et al., 1990; Wilde et al., 1996). Only the sample ZOM 5 shows a positive Ce anomaly ($Ce/Ce^* = 1.30$), whereas the remaining samples have slightly negative anomalies ($Ce/Ce^* = 0.88-0.96$) (Table 3; Fig. 5), which may reflect less reducing conditions in sample ZOM 5.

Interrelating the Eu and Ce anomalies, samples ZOM 16 and ZOM 5 seem to be related to more oxidizing environments, whereas the other samples seem to be deposited in more reducing depositional conditions (Fig. 10).

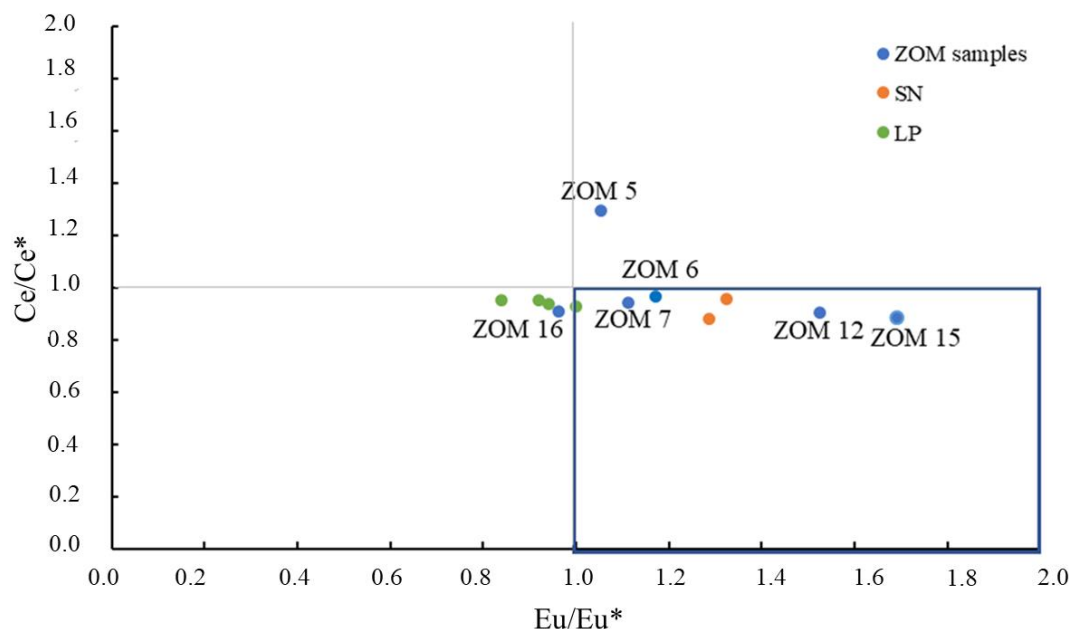


Figure 10 - Ce/Ce^* and Eu/Eu^* cross plot considering the studied samples and from samples of *Série Negra* of OMZ studied by Pereira et al. (2006) and Lopes (2015) containing graphite (SN and LP, respectively). The highlighted field represents a more reducing depositional conditions.

All the used ratios (Table 6), as well as the Ce and Eu anomalies, revealed that the samples ZOM 6 and ZOM 12, and secondarily the sample ZOM 15, were deposited under anoxic conditions, whereas the other samples were deposited in more oxidizing conditions, although with dissimilar paleoredox conditions. This is consistent with the TOC values that are higher in ZOM 6 and ZOM 12, in which the redox conditions favored the OM preservation, and the increase of some redox sensitive elements (e.g. Mo, U, V). Samples ZOM 5, ZOM 7 and ZOM 15 behave consistently presenting lower TOC values

(< 1 %), and redox sensitive proxies pointing to more oxic to suboxic depositional conditions. The same pattern was found for organic-rich pelites and metasedimentary lithologies with graphite from the *Série Negra* of OMZ (Pereira et al., 2006; Lopes, 2015).

Therefore, the *Série Negra* succession can be interpreted as related to the erosion of the Cadomian magmatic-arc, being deposited in proximal back-arc basin. The geochemical composition of black shales from this succession indicates discrepant anoxic conditions, which can be interpreted as resulting from the variation of paleoredox conditions within the back-arc basin generated during the last episodes of the magmatic-arc inception.

2.4.3. *Série Negra* as possible source of metals

The diversity of ore deposits and mineral occurrences in OMZ result from a complex tectono-metamorphic evolution derived from the location of the OMZ within Iberian Massif and the existence of several magmatic-hydrothermal events during the Cadomian and Variscan Cycles (Liñán and Quesada, 1990; Tornos et al., 2004).

The tectono-metamorphic, magmatic, and depositional processes have certainly controlled the genesis of many ore deposits in OMZ (Tornos et al., 2002). Indeed, the OMZ is characterized by significant crustal heterogeneities (Locutura et al., 1990), which imposes variations in the composition of the metal reservoir, and the multiple tectono-metamorphic and magmatic-hydrothermal processes that might have conditioned the transport and precipitation of the metals (Tornos et al., 2004), thus reflecting the differences between the metallogenic belts within this tectonostratigraphic domain. Therefore, the OMZ displays a great variety of ore occurrences, including Fe, Pb-Zn, Cu, Au, Ag, Sb, Ni, Mn, W, Hg, U and REE, among others, which are formed by different processes in distinct geological settings and times (Tornos et al., 2004).

Some Au occurrences are reported in OMZ (Fig. 1A), namely in the Arronches-Córdoba Belt (Mosteiros - Nave de Grou and São Martinho - Blastomylonitic Belt), Évora - Aracena Belt (Boa Fé-Escoural), and in the Olivenza - Monesterio Belt (Guijarro and Chocolateiro) (Canales and Matas, 1992; Tornos et al., 2004; Matos and Filipe, 2013). These occurrences are considered as orogenic Au deposits, controlled by major shear zones. They are characterized by sulfide-poor quartz-bearing veins, breccias and disseminations in a host-rock, and have been interpreted as Variscan syn-metamorphic mineralizations (Oliveira et al., 2007; Tornos et al., 2004; Maia et al., 2022).

In Alter do Chão - Elvas and Estremoz Anticline Sectors (Central Belt), several Cu mineralizations are present (Matos and Filipe, 2013), most of these mineralizations are interpreted as late Variscan Cu-Veins (Mateus et al., 2013; Maia et al., 2020) hosted in Paleozoic successions. In the North - Central Belt (Alter do Chão - Elvas sector) most of Cu, Zn and Pb occurrences are hosted in Lower Cambrian Succession (Oliveira, 1986; Mateus et al., 2013), being concurrently described some Au and Ag enrichments in similar occurrences in Spain (Tornos et al., 2004).

Figure 11 shows the enrichment of selected elements that may have affinity with Au, Pb, Zn and Cu, namely, Ag, As, Bi, Cd, Co, Cr, Mo, Ni, Sb, Se, U and V (Huyck, 1989; Large et al., 2011). Although the Au content was not analyzed in the studied samples, several elements have a geochemical affinity with Au, and can be used as proxies to discuss the potential presence of Au. All samples present a significant enrichment in As and Se, both with strong affinity with Au (Large et al., 2011). Samples ZOM 6 and ZOM 12, with higher TOC, also shows significant enrichment in Bi and Mo, in addition to Ag and Cu on sample ZOM 6 and Sb on sample ZOM 12. The presence and relative enrichment of these elements in the mentioned samples could be indicative of primary presence of Au. Furthermore, samples ZOM 6 and ZOM 12 are associated with anoxic to suboxic environments, which favor the formation of significant amounts of diagenetic pyrite (Tribovillard et al., 2006; Large et al., 2011), although diagenetic pyrite can form in a wide range of conditions. It is noteworthy that the petrographic and SEM observations (Laranjeira et al., 2023) reveal the presence of pyrite crystals in sample ZOM 6.

Previous studies on OM-rich sediments showed that some Au deposits have a strong positive correlation with As and S contents (Large et al., 2011). In reduced continental margin basin settings, the OM-rich sediments deposited under anoxic to euxinic conditions concentrate Au, As, S, and other trace elements such as Ag, Cu, Mo, Ni, Se, Te, V, U, and Zn in pyrite and arsenopyrite phases (Tribovillard et al., 2006; Large et al., 2011). It is plausible that successive tectono-metamorphic processes, namely the Variscan shear zones, could remobilize Au, As, S and other elements (e.g. Bi, Cu, Mo, Pb, Sb, Te, Tl and Zn) from these OM-rich sediments to become concentrated by hydrothermal processes (Large et al., 2011).

Indeed, Tornos et al. (2004) suggest that OMZ orogenic Au mineralizations were probably formed by hydrothermal/metamorphic fluids that leached Au contained in the *Série Negra* succession, in accordance with recent data from Maia et al. (2022) which suggest that the Neoproterozoic metasediments were the most probable suppliers of S and Au to the system. Therefore, the hydrothermal/metamorphic fluids related to

Variscan transpressional shear zones may remobilize the Au content within black shales from *Serie Negra* succession, thus enabling the genesis of quartz-bearing veins and stockworks with a possible enrichment in Au. However, it must be emphasized that not all *Serie Negra* succession lithotypes have a propensity to be an Au source. Indeed, only the black shales deposited in most anoxic environments (ZOM 6 and ZOM 12) seem to show an increase of content in elements with significant Au geochemical affinity.

If it is considered that the black shales of the *Série Negra* succession have a primary Au content, the depleted pattern of some samples (e.g., ZOM 7) may be interpreted as related to the remobilization of metals during Tomar - Badajoz - Córdoba shear events (Pereira et al., 2010; Pereira et al., 2012b). Those remobilized metals may be focused, and the shear zone activity may form extensional structures, that allowed the precipitation of metals and, consequently, the genesis of some Au occurrences in the OMZ high grade domains (e.g., Montemor-o-Novo region and Blastomylonitic Belt).

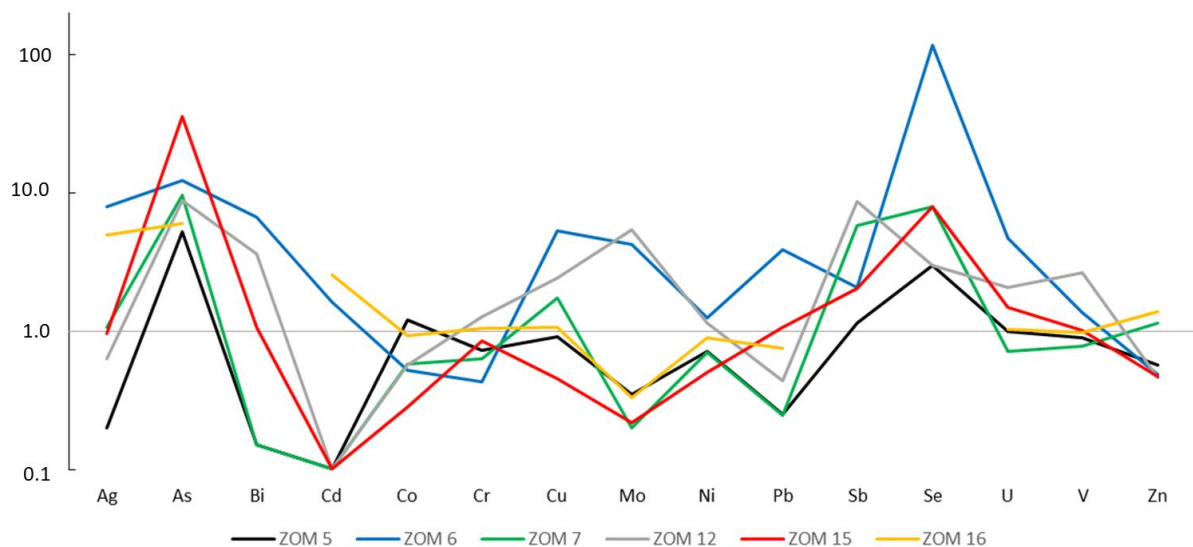


Figure 11 - Selected elements with possible affinity with Au, Pb, Zn and Cu normalized to PAAS (Taylor and McLennan, 1985; Condie, 1993).

Near the location where samples ZOM 5, ZOM 6 and ZOM 16 were collected, an occurrence of Pb-Zn is known, possibly related to late hydrothermal processes associated with the emplacement of Santa Eulália Plutonic Complex (Fig. 1A). This fact may explain the enrichment in Pb content in sample ZOM 6 relatively to the remaining

samples. However, this increase could also be primary, because the other samples from this location (ZOM 5 and ZOM 16) do not show similar behavior.

Sample ZOM 12 is located near some Cu occurrences (Fig. 1A). According to what was previously demonstrated by the paleoredox ratios, sample ZOM 12 corresponds to suboxic to anoxic paleoenvironmental conditions and has a significant enrichment in Ag, As, Bi, Cu, Mo, Sb, Se, U and V (Table 4; Fig. 11). The positive correlations between TOC and some redox-sensitive elements, and specifically with Cu ($r = 0.80$) corroborates their formation and Cu enrichment formed under suboxic to anoxic conditions.

2.5. Conclusions

Black shales from *Série Negra* succession of OMZ were studied using a petrographic, geochemical and mineralogical approach for the characterization of the OM present in the black shales, and to trace the depositional paleoenvironments and the possible sources based on redox sensitive elements.

The petrographic observations reveal the presence of organic particles of variable size and shape in all samples. The TOC content varies between 0.20% and 1.53%, and only three of the studied samples have TOC content higher than 0.5%, thus being considered black shales. The reflectance indicates the presence of organic particles of anthracite to semi-graphite, formed during the graphitization, at temperatures above 300 °C and P, accompanying the burial experienced by the sediments in the basin and metamorphic/metasomatic processes.

The results of geochemical and mineralogical analysis indicate that the metal occurrences on OMZ and the black shales from *Série Negra* succession seems to be linked. The clastic sources of the studied black shales are related with the dismantling of the Cadomian Continental Arc developed in the North Gondwana margin, showing acidic to mixed felsic/basic signatures, which is in accordance with previous proposed models.

The CC considering different reference materials reveal an enrichment ($CC > 2$) in several elements: Ag, As, Cs, Ba, Bi, Cd, Cu, Mo, Pb, Sb, Sn, Se, Th, Ti, U, V, and LREE. Samples ZOM 6, ZOM 12, and ZOM 15 have the high number of enriched elements. Some samples reveal $CC > 10$ for Ag, As, Bi, and Se. Based on Pearson's correlation coefficient and considering the significant positive correlations between TOC and S, it is demonstrated the association of OM with the occurrence of sulfides, corroborating the petrographic description of the samples. The elements Ag, Cd, Cu, Pb and Se are

thought to be preferentially associated with sulfides, while the elements Mo and U must be preferentially organically bound. The Eu positive anomaly, the Ce negative anomaly and the ratios calculated based on redox sensitive elements indicate oxic to anoxic paleoenvironmental conditions, being more noticeable the anoxic conditions in samples ZOM 6 and ZOM 12, which are also the samples with highest TOC values. Those samples are enriched in Ag, As, Bi, Co, Cu, Mo, Sb and Se indicating that the BS deposited in anoxic environment and may represent an important source of metals as proposed by other authors.

CHAPTER 3

SILURIAN BLACK
SHALES FROM OSSA-
MORENA ZONE

Silurian black shales from Sousel-Barrancos metallogenic belt (Ossa-Morena Zone, Portugal): characterization and interplay to Cu deposits

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Abstract

Black shales are commonly spatially associated with metal-rich deposits, wherein organic matter may in these rocks may condition or or influence the processes related with the concentration of metals and formation of ore deposits. In the Ossa-Morena Zone (South of Portugal), namely in the Sousel-Barrancos metallogenic belt, several Cu mineralized veins occurs, being generally hosted in Silurian metasedimentary units mainly composed of black to grey shales, with interbedded lydrites and black quartzites. This research aims to contribute to the study of the association between those Silurian black shales and the Cu ore deposition in the Sousel-Barrancos metallogenic belt. The petrographic, geochemical, and mineralogical analysis of black shales was performed to characterize the organic and inorganic fractions, to investigate elements concentration and its mode of occurrence. The data allow to identify the spatial pattern of thermal maturation of these black shales related to the variability of metamorphic processes, and the studied samples collected in drill cores from Miguel Vacas deposit also allow to identify an irregular pattern of maturation associated to the pathway of hydrothermal fluids. A significant Cu enrichment in black shales in the supergene enrichment domains were identified and data seems to indicate that Cu concentration is not directly related with organic carbon content, probably indicating a distinct source for Cu content. The mobilization of hydrothermal fluids, possibly of magmatic source, contributed to the discrepant maturation of organic matter in black shales.

3.1. Geological setting

The OMZ is a tectonostratigraphic zone of the Iberian Massif (Fig. 12A), showing differentiated stratigraphic, magmatic, and structural features (e.g., Ribeiro et al., 2007; Moreira et al., 2014; Quesada and Oliveira, 2019). The complex and multicycle evolution of this zone is also recorded in its metallogenic features, generating several small-scale ore deposits, including syn-sedimentary, syn-metamorphic and syn-magmatic deposits controlled either by Cadomian or Variscan cycles (Tornos et al., 2004; Mateus et al., 2013): base metal-bearing veins, polymetallic massive sulfide deposits, Fe-skarns, magnetite and Cu-Ni magmatic ore bodies, among others. The spatial disposition and the metallogenic models of those mineralizations allowed to discriminate several metallogenic belts in the OMZ (Fig. 12B).

In central OMZ, namely in Sousel-Barrancos metallogenic belt, several Cu-Fe ($\pm$ Zn $\pm$ Pb $\pm$ Au) vein occurrences and deposits are known, that share common features. The Cu-Fe veins are composed of quartz-carbonate and sulfides, being hosted in Paleozoic metasedimentary series (Mateus et al., 2003; 2013; Maia et al., 2019; 2020). Several of these Cu-Fe veins were object of exploitation, during the 19th and 20th centuries (e.g., Oliveira, 1984, 1986; Matos and Rosa, 2001; Mateus et al., 2003; 2013; Tornos et al., 2004).

In the Sousel-Barrancos belt, there are two important clusters of Cu occurrences (Figs. 12B and 12C): (1) Alandroal cluster, where the Bugalho, Zambujeira, Miguel Vacas and Mociços (Fig. 13A) mines are located, and (2) Barrancos cluster, where the Minancos, Aparis, Botefa and Defesa das Mercês mines are placed (Fig. 13B) (Matos and Filipe, 2013; Mateus et al., 2013).

Those fault-controlled Cu veins were developed along several trends, being described NNW-SSE, NNE-SSW and ENE-WSW veins, being also developed along the NW-SE regional trend. These structures comprise polyphase, brecciated hydrothermal infillings, composed of quartz, carbonates (dolomite, ankerite, siderite and calcite), sulfides (chalcopyrite, pyrite, arsenopyrite, sphalerite, pyrrhotite and galena) and sulfosalt minerals (tetrahedrite-tenantite) (Mateus et al., 2013). Supergenic enrichment processes are also common, leading to the development of mineral associations consisting of iron (hydr-)oxides, malachite and azurite, cuprite and other secondary Cu minerals (Mateus et al., 2013).

As aforementioned, the veins cut the Paleozoic metasedimentary successions, namely Ordovician to Lower Devonian units (Fig. 13B). Nevertheless, most of veins are hosted in black to grey shales, sometimes with interbedded lydites and black quartzites (Oliveira, 1986; Mateus et al., 2013) of Silurian to Lower Devonian age (*Xistos com Nódulos* and *Xistos Raiados* Formations; Fig. 12). The presence of disseminated sulfides is also a common feature on the Silurian black shales (Oliveira, 1986).

As respect to the genesis of these veins, it is considered that mineralized structures are related with hydrothermal activity contemporaneous of late Variscan brittle deformation stages (Oliveira, 1984; Mateus et al., 2003, 2013; Maia et al., 2019; 2020).

According to some authors (Oliveira, 1986; Mateus et al., 2003, 2013; Tornos et al., 2004), the Cu content is considered to be a result of remobilization from the metasedimentary succession, specifically from the Silurian succession which contains OM deposited in euxinic conditions (Piçarra, 2000; Araújo et al., 2013, Roseiro et al., 2020). Other authors (Tornos et al., 2004; Mateus et al., 2013) also emphasizes the presence of anomalous Au concentration in some those Cu dykes (Defesa das Mercês and Mostardeira), discussing a possible volcanogenic primary source of metals. Recently, Maia et al. (2020) highlights the presence of magmatic-hydrothermal derived fluids related with Cu vein deposits in Sousel-Barrancos metallogenic belt. The authors hypothesized the existence of a deep-seated magmatic body as possible source of hydrothermal fluids (and metals?), however not excluding the possibility that Paleozoic metasedimentary units contributed as a metal source for ore deposits.

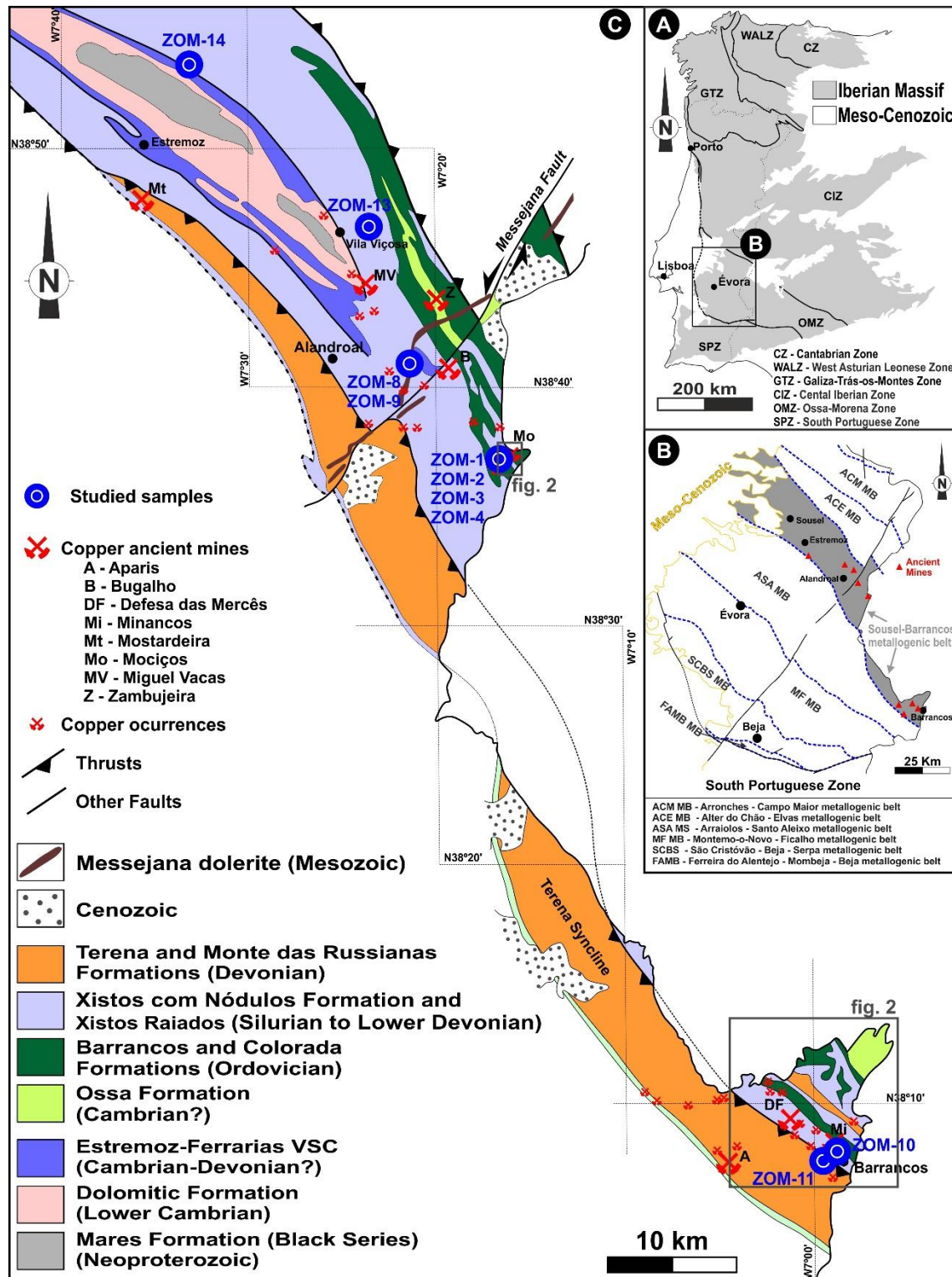


Figure 12 - A) OMZ localization on Iberian Massif context (LNEG, 2010); B) Representation of the different metallogenic zones of OMZ (adapted from Oliveira, 1986; Mateus et al., 2013); C) Location of Cu mines and occurrences in the Sousel-Barrancos Metallogenic Belt (adapted from Matos and Filipe, 2013).

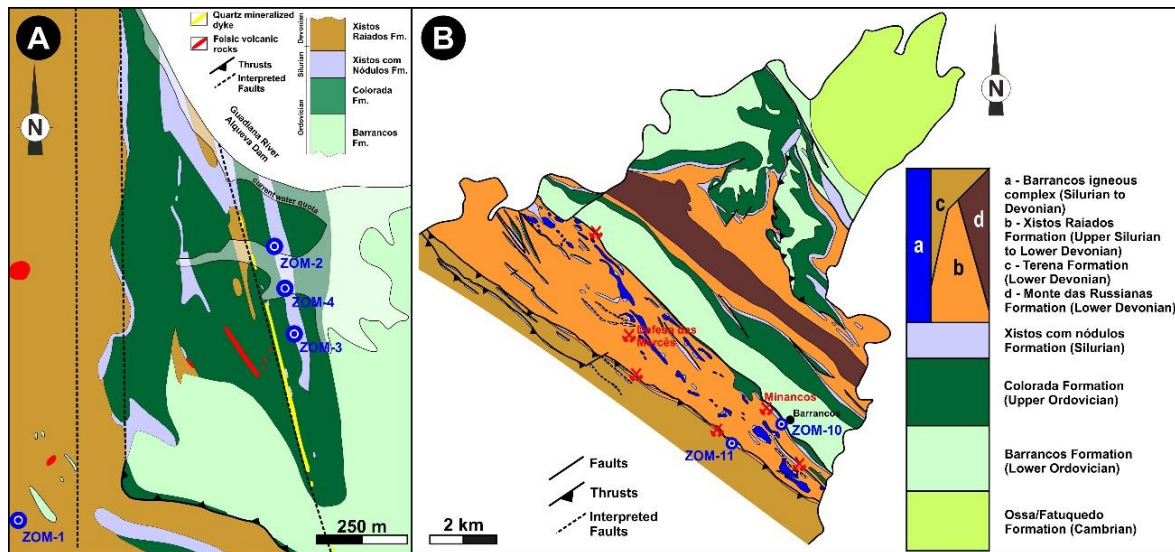


Figure 13 - A) Geological map of the Mociços mine (adapted from maps of the Serviço de Fomento Mineiro, Vitor Oliveira); B) Geological map of the Barrancos region with the location of the Minancos mine (adapted from Piçarra, 2000 and Araújo et al., 2013).

The Miguel Vacas Cu vein case study

In the Sousel-Barrancos metallogenic belt there are several Cu-rich vein ancient mines (e.g., Mociços or Miguel Vacas) and occurrences (e.g., Ferrarias). The Miguel Vacas mine, located in the Alandroal cluster (5 km SE from Vila Viçosa - district of Évora; Fig. 12C), is an ancient mine that was exploited as an open pit, but in the initial phase was exploited underground (Figs. 14A, 14B, and 14C). The mining activities lasted between 1925 and 1986 (Fernandes, 2012).

The Miguel Vacas mine exploited an array of Cu veins that occur in the NE limb of the Estremoz Anticline (Fig. 12), being hosted in the Silurian metasedimentary succession (Fig. 15; *Xistos com Nódulos* Formation), mainly composed of black to grey shales (Oliveira, 1986; Tornos et al., 2004; Corrula and Branco, 2005; Mateus et al., 2013), with low grade metamorphism, not exceeding the greenschist facies in the chlorite-biotite zones (Oliveira, 1984; Pereira et al., 2012; Moreira et al., 2019). It is an anastomosing vein structure that extends over 2000 m in length, with an NNW-SSE direction, and dipping 50° - 80° to E, presenting variable thickness between 10 and 20 m (Corrula and Branco, 2005; Fernandes, 2012).

The Miguel Vacas Cu vein is mostly composed of fault breccias, including heterometric, angular and hydrothermally altered fragments of diverse shale host rocks, and quartz breccias (Fig. 15; Mateus et al., 2003; Fernandes, 2012). Prospecting works carried out

during the 20th century, recognize the mineralization until 330 m in depth and the first 80-90 m corresponding to a horizon of supergene metal-enrichment, being the primary Cu sulfides mineralization at higher depths (Mateus et al., 2003; Fernandes, 2012).

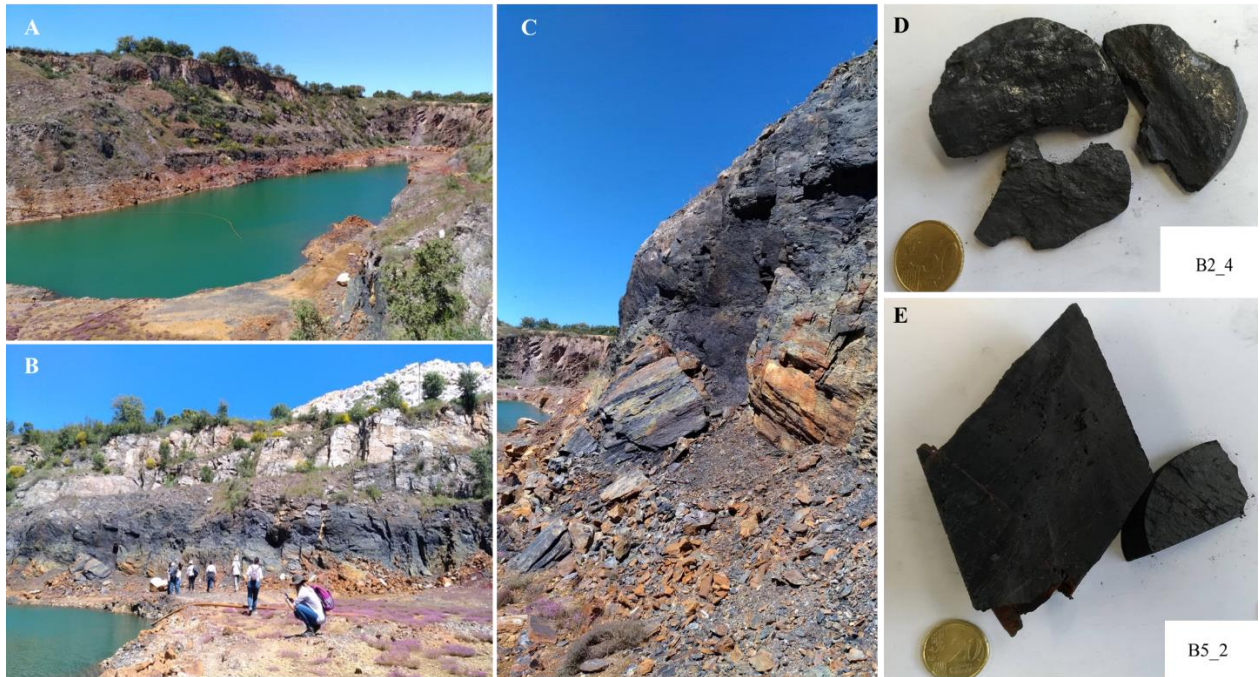


Figure 14 - A) Miguel Vacas open pit mine; B) and C) Miguel Vacas outcrops with visible black shales; D) and E) Examples of samples selected from drill cores of boreholes executed in Miguel Vacas area.

The primary ore (deepest zone) is mainly composed of sulfides (chalcopyrite, pyrite and arsenopyrite) associated with fault breccias containing quartz and carbonates ($\text{cal} \pm \text{ank} \pm \text{sd}$) (Mateus et al., 2003; 2013; Fernandes, 2012). In contrast, the supergenic enrichment domain (superficial zone), which results from a horizon where a strong oxidation and hydration occurred, is composed of a combination of secondary Cu minerals such as, carbonates (malachite and azurite), phosphates (libethenite and pseudomalachite), sulfates (brochantite), sulfides (cuprite, chalcocite, bornite, covellite) and native Cu, associated with some Bi mineral phases (Fernandes, 2012).

Beyond the significant Cu content, Miguel Vacas veins also show a significant content of Au (Mateus et al., 2003), although occurs erratically throughout the profile, probably because it occurs as microinclusions both in the primary and secondary sulfide phases (Fernandes, 2012).

3.2. Sampling

A total of 39 samples of Silurian black shales from Sousel-Barrancos metallogenic belt were studied: 10 from outcrops and 29 from drill cores. Samples from drill cores were collected in five boreholes performed by a private company for exploration in the Miguel Vacas Cu deposit during 2014 and 2015, being selected from different depths. The outcrop samples of black shales were mainly collected in Alandroal region (8 samples). From these, 4 samples were collected in outcrops near Mociços ancient mine and 2 samples near the Ferrarias occurrence. Other 2 outcrop samples were collected in Barrancos region, far from Cu occurrences. The samples collected far from the mineralizations may provide information from the background of the Sousel-Barrancos metallogenic belt Silurian black shales without the influence of mineralizing processes. Table 7 shows supplementary information about the collected samples.

Table 7 - Systematization of sampling information.

Region	Samples
Alandroal - Mociços (outcrops)	ZOM 1, ZOM 2, ZOM 3, ZOM 4 (near the mineralization)
Alandroal - Ferrarias (outcrops)	ZOM 8, ZOM 9 (near the mineralization)
Alandroal (outcrops)	ZOM 13, ZOM 14 (far from the mineralization)
Alandroal - Miguel Vacas (drill cores)	B1 (84.1 m depth, 45° inclination): 5 samples (B1_1 to B1_5) B2 (144 m depth, 50° inclination): 6 samples (B2_1 to B2_6) B3 (109 m depth, 45° inclination): 5 samples (B3_1 to B3_5) B4 (195 m depth, 60° inclination): 6 samples (B4_1 to B4_6) B5 (152 m depth, 45° inclination): 7 samples (B5_1 to B5_7)
Barrancos (outcrops)	ZOM 10, ZOM 11 (far from the mineralization)

During sampling in the outcrops, the superficial layers have been removed to avoid weathered material. The boreholes executed in Miguel Vacas mine area (Fig. 15) allow sampling along the drill cores, being selected fragments of black shales from different depths without evidences of weathering (Figs. 14D and 14E). Figure 16 presents the logging details adapted from the information provided by the company. The proximity to mineralized veins was considered in the samples selection, in accordance with the logging information. The samples considered proximal to mineralized veins are located up to a maximum of 10 m from the mineralized veins (Fig. 16).

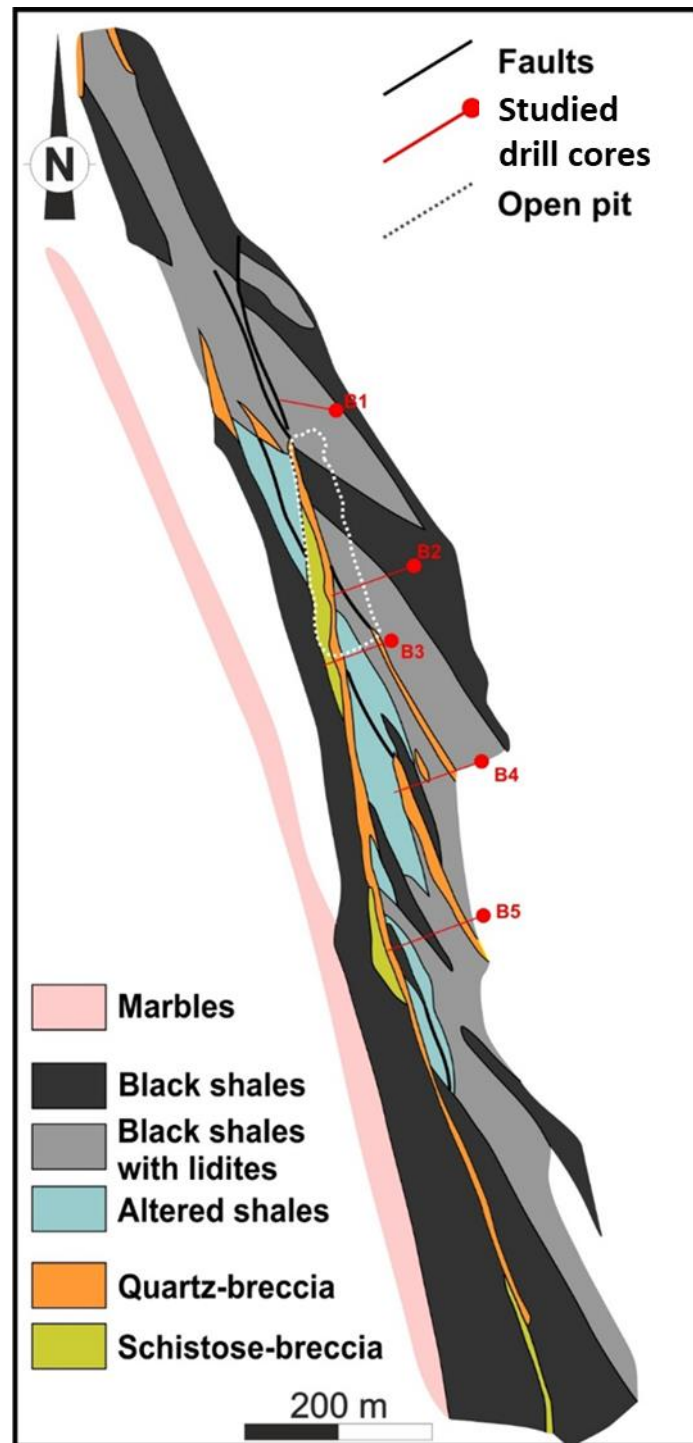


Figure 15 - Geological map of the Miguel Vacas deposit and location of the boreholes (adapted from Corrula and Branco, 2005).

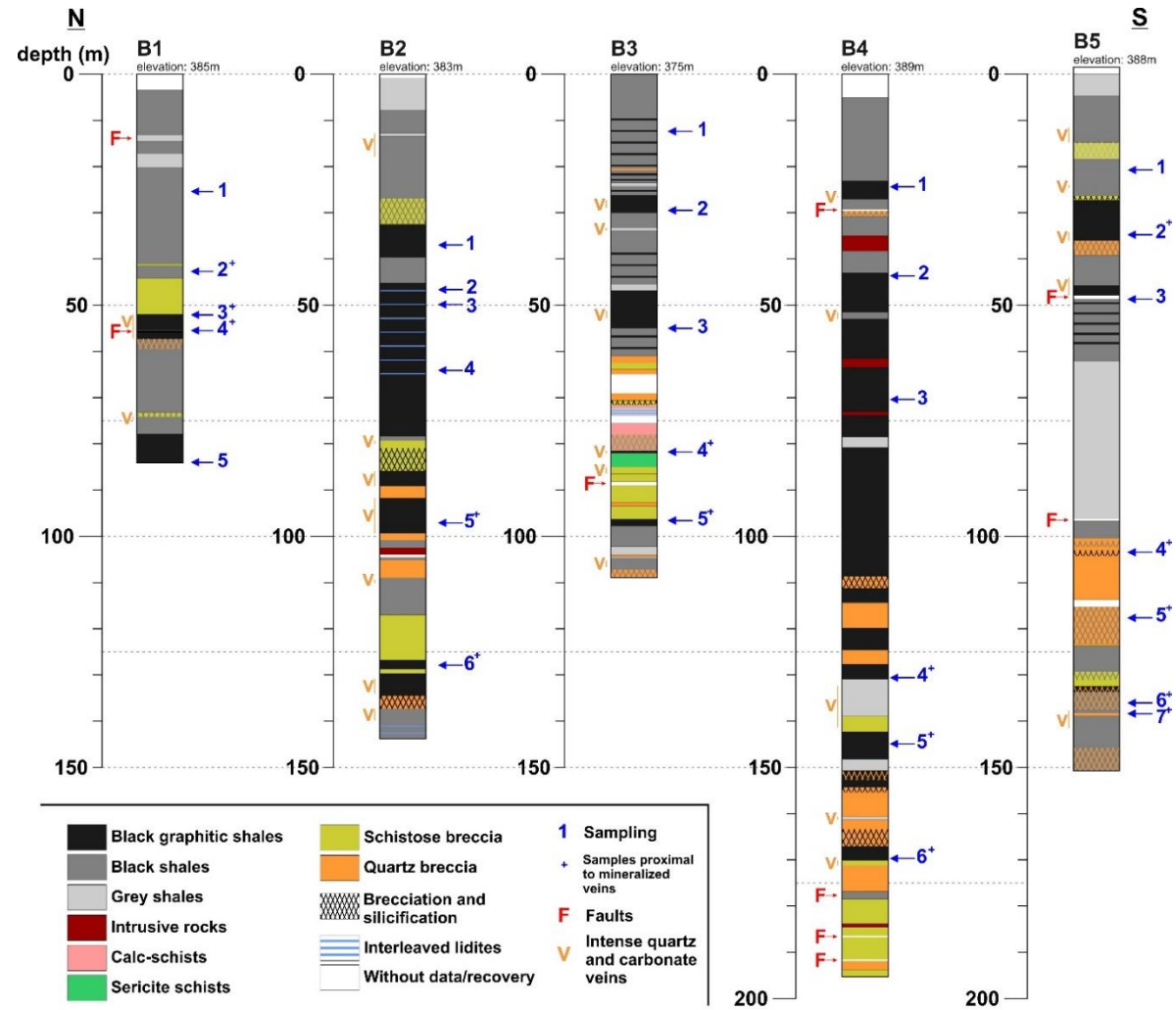


Figure 16 - Geological logging of the boreholes and identification of selected black shale samples for study (samples proximal to mineralized veins are marked in this figure and in the manuscript with the symbol +).

3.3. Results

3.3.1. Petrographic characterization of organic and inorganic matter

- Alandroal and Barrancos outcrop samples

The petrographic observations of the Silurian black shales allowed the identification of vitrinite-like particles in all samples, all of them without evidence of weathering. The organic particles are generally thin and elongated, occurring, essentially, interbedded in the mineral matter (Figs. 17, 18 and 19). Organic particles are more abundant in sample ZOM 2, from the Alandroal area, and in sample ZOM 10, in the Barrancos area. In some samples from Alandroal area, near mineralized domains (ZOM 1, ZOM 2, ZOM 3, ZOM 4, ZOM 8 and ZOM 9) and the ones far from mineralization (ZOM 13 and ZOM 14), were observed vitrinite-like particles exhibiting single flakes graphitic features were observed (Figs. 17A to 17F).

Some undifferentiated zooclasts were identified in samples ZOM 3 and ZOM 4 (Figs. 18A and 18B). The OM can be classified as zooclasts when some distinguished specific morphological characteristics are observed, e.g., fish spines and scales, arthropod exoskeletal debris, insect cuticles fragments, organic linings from bivalve shells, ostracod carapaces, graptolite fragments or crustacean eggs (Mendonça Filho and Gonçalves, 2017).

In samples from Barrancos (ZOM 10 and ZOM 11), remains of graptolites were identified (Figs. 18C to 18F). Graptolites are organic fossils that occur mainly in Lower Paleozoic (from Ordovician to Lower Devonian) (Goodarzi, 1984, 1985; Goodarzi and Norford, 1987), being abundant in black shales, siliceous shales and cherts, and are characteristic of external shelf to deep ocean environments (Cooper et al., 2012). Petrographically, under reflected light, graptolites can be distinguished by their characteristics, such as granularity, fusellar layer, anisotropy (Goodarzi, 1984, 1985; Goodarzi and Norford, 1987; Petersen et al., 2013; Luo et al., 2016; Gonçalves et al., 2020) and can show two different types of texture:

- Granular texture - graptolites show a fine granular to reticular form, are anisotropic (Goodarzi, 1984; Goodarzi et al., 1992, Gonçalves et al., 2020) and can be found mainly in carbonates (Goodarzi, 1984; Goodarzi and Norford, 1987; Petersen et al., 2013).

- Non-granular texture - it was described as presenting higher reflectance, strong anisotropy and are more common in shales (Goodarzi, 1984; Goodarzi and Norford, 1987; Petersen et al., 2013; Gonçalves et al., 2020).

In samples from Barrancos (ZOM 10 and ZOM 11), the fragments of graptolites are large compared to other organic particles, showing an elongated rectangular shape and usually presenting segmentation (Figs. 18D and 18E). Fragments of graptolites show a higher reflectance and anisotropy than other particles of OM, being possible to identify the non-granular texture. The abundance of graptolites in Barrancos area had already been noted (Piçarra, 2000).

The petrographic analysis also allows the observation of detrital silicate minerals occurring in association with OM. In Alandroal samples collected near Cu occurrences, the mineral matter is different among the studied samples: in ZOM 1, ZOM 3 and ZOM 8 is possible to observe abundant iron oxides (Figs. 17A, 17C, 18A and 19A), in ZOM 4 the presence of sulfides is noticeable, and in ZOM 2 and ZOM 9 a more siliceous material is noted.

Otherwise, the samples collected in the Alandroal area, far from Cu occurrences, show more siliceous components in ZOM 14 (Fig. 19B) and the noticeable presence of iron oxides on ZOM 13 (Fig. 17E). Samples from Barrancos (ZOM 10 and ZOM 11) show a significant difference compared with others; they have less iron oxides and consist essentially of aluminosilicates and OM (Figs. 18C to 18F).

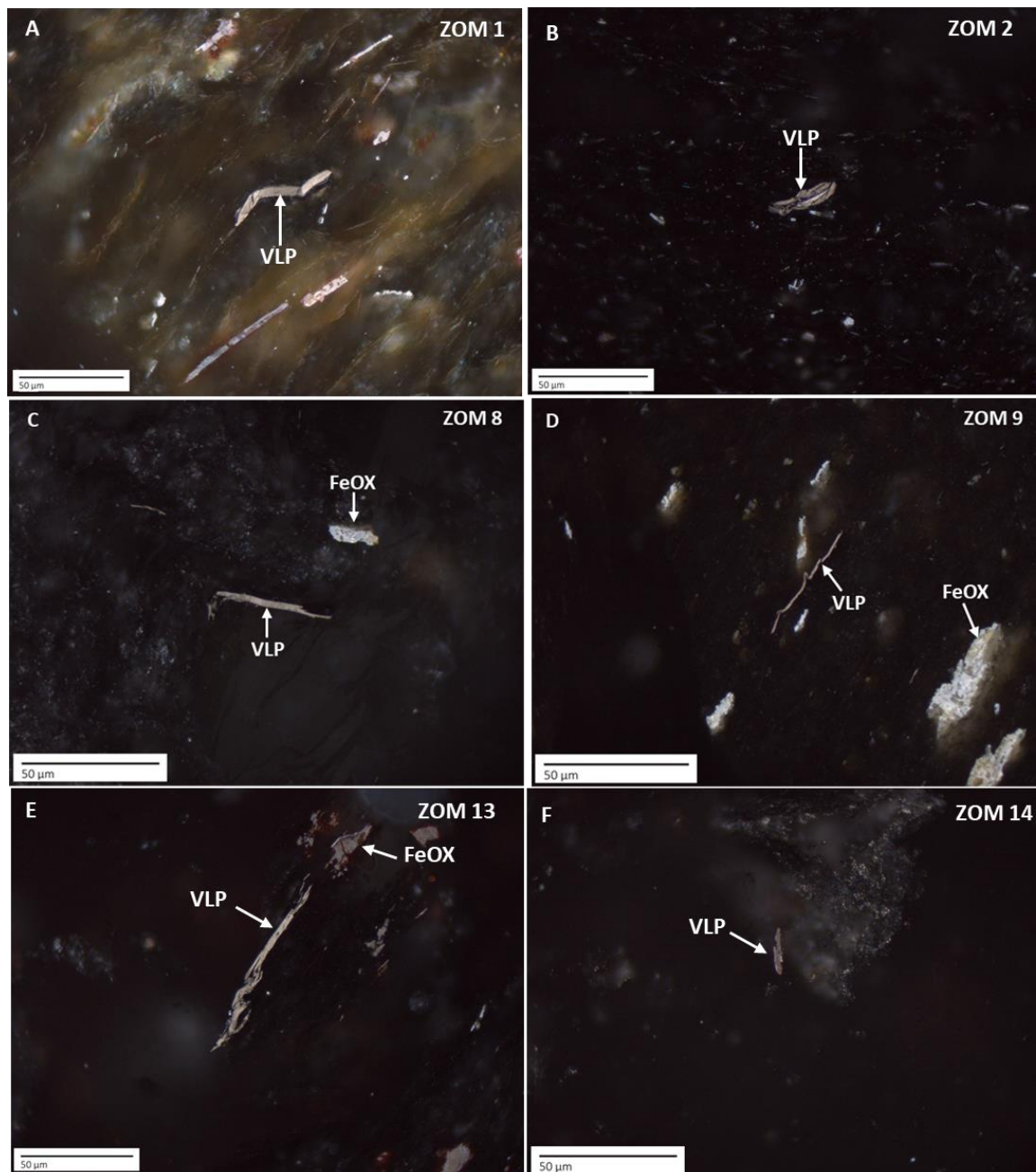


Figure 17 - Photomicrographs of the studied samples from: A) and B) Alandroal area near the mineralization exhibiting vitrinite-like particles (VLP) showing single flakes graphitic characteristics and iron oxides (FeOX), occurring within mineral matter; C) and D) Alandroal area near the mineralization exhibiting vitrinite-like particles (VLP) thin and elongated, essentially isolated, and some iron oxides (FeOX) particles; and E) and F) Alandroal area far from the mineralization exhibiting vitrinite-like particles (VLP) displaying single flakes graphitic features and iron oxides (FeOX). Photomicrographs taken in reflected white light and 50x immersion oil objective.



Figure 18 - A) and B) Photomicrographs of the samples from Alandroal area near the mineralization presenting fragments of zooclasts and iron oxides (FeOX) particles; C), D), E) and F) Photomicrographs of the samples from Barrancos displaying graptolites (Grap). Photomicrographs taken in reflected white light and 50x immersion oil objective.

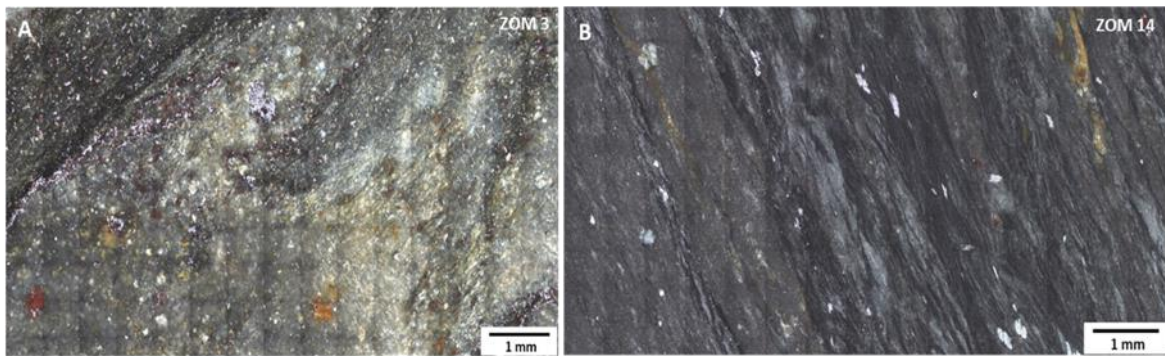


Figure 19 - Mosaics prepared from the assembly of photomicrographs taken from the polished blocks of rock pieces, exhibiting a general petrographic view and main features of samples ZOM 3 and ZOM 14.

Photomicrographs taken in reflected white light and 20x immersion oil objective.

- Miguel Vacas occurrence

Samples from Miguel Vacas allow to identify vitrinite-like particles in all samples, and generally they are thin and small in size, with varied morphology, and occur interbedded with mineral matter (Figs. 20A, 20B and 20C). Larger organic particles exhibiting graphitic structures are also observed in some samples, occurring as single flakes disseminated in fragments of interbedded mineral and OM (Figs. 20D, 20E and 20F).

Additionally, graptolites (Figs. 21A to 21F) are also present in some samples; the fragments of graptolites found in samples B2_2, B2_3, B3_1, B3_2, and B5_2 are large compared to vitrinite-like particles, show an elongated rectangular shape and are segmented. They are interbedded with mineral matter, present non-granular texture and strong anisotropy.

It was possible to observe some differences in the mode of occurrence of OM between the different drill cores. In B1 the presence of particles exhibiting graphitic structures is more significant (Figs. 20D and 20E). In B2 were identified fragments of graptolites in two samples (B2_2 and B2_3) and, in general, the OM also occurs in massive particles interbedded with mineral matter (Fig. 20A). In samples from B3 and B4 drill cores, the OM is very similar, also occurring in larger massive particles with thin OM embedded with minerals (Fig. 20C).

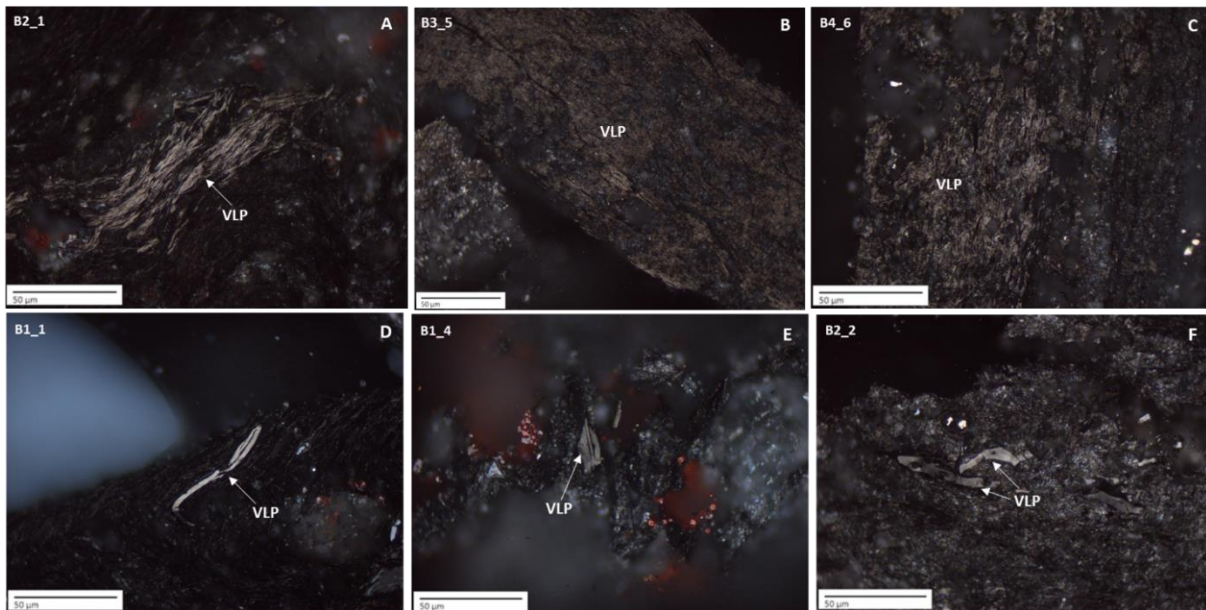


Figure 20 - A), B) and C) Photomicrographs showing the vitrinite-like particles (VLP), occurring interbedded along mineral matter; D), E) and F) Photomicrographs of vitrinite-like particles (VLP) exhibiting graphitic structures occurring as single flakes. Photomicrographs taken in reflected white light and 50x immersion oil objective.

Graptolites are observed in samples B3_1 and B3_2 (Figs. 21C, 21D and 21E), while in the B4 were not identified. Samples from B5 have the lowest amount of organic particles when compared with samples from the other drill cores; fragments of graptolites were observed in one sample (B5_2) (Fig. 21F).

The inorganic fraction is essentially composed of detrital derived minerals (mainly silicate minerals) and the presence of iron oxides is common (Fig. 22). In samples from drill cores B1 and B3, there is a greater presence of iron oxides when compared to the samples from the other drill cores (Figs. 22A and 23A), while samples from B2 and B5 presents more siliceous components (Fig. 23B). Samples from B4 stand out due to the presence of abundant sulfides, mainly in samples located near to the mineralized veins (Figs. 23C and 23D).

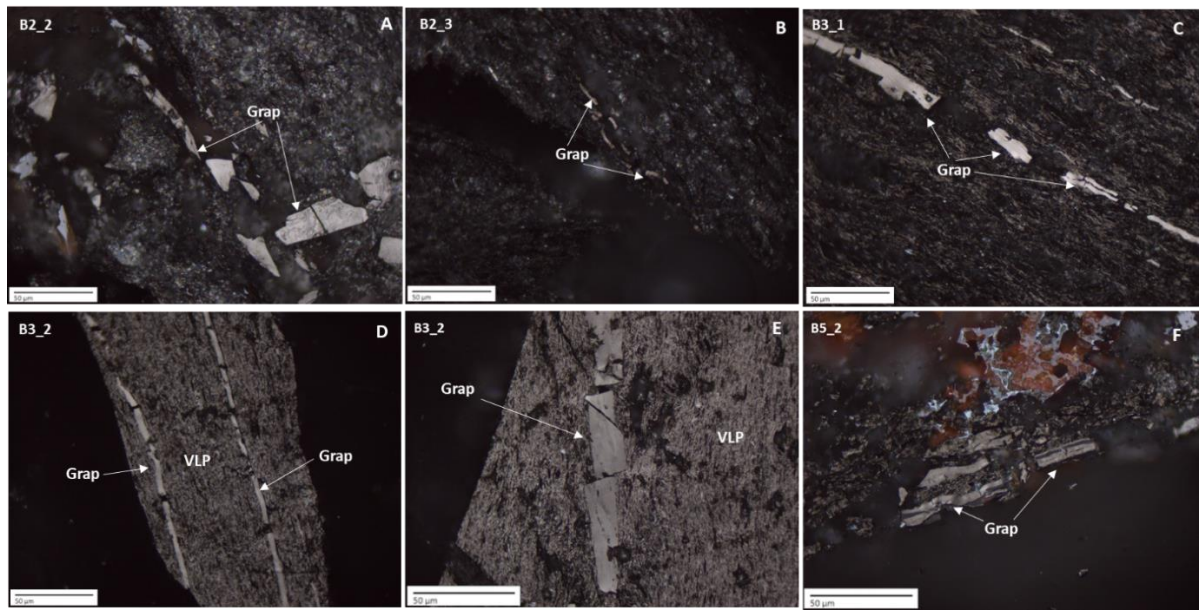


Figure 21 - A) to F) Photomicrographs showing graptolite fragments (Grap) interbedded with vitrinite-like particles (VLP) and mineral matter. Photomicrographs taken in reflected white light and 50x immersion oil objective.

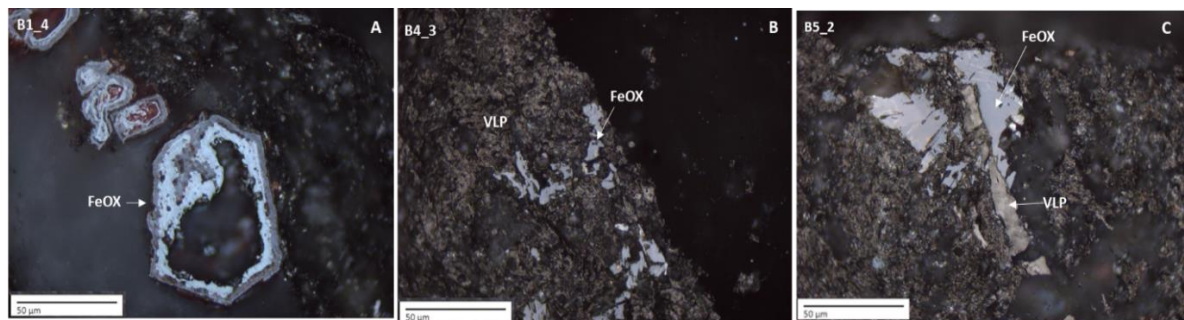


Figure 22 - A) to C) Photomicrographs of the presence of iron oxides (FeOX) interbedded with vitrinite-like particles (VLP). Photomicrographs taken in reflected white light and 50x immersion oil objective.

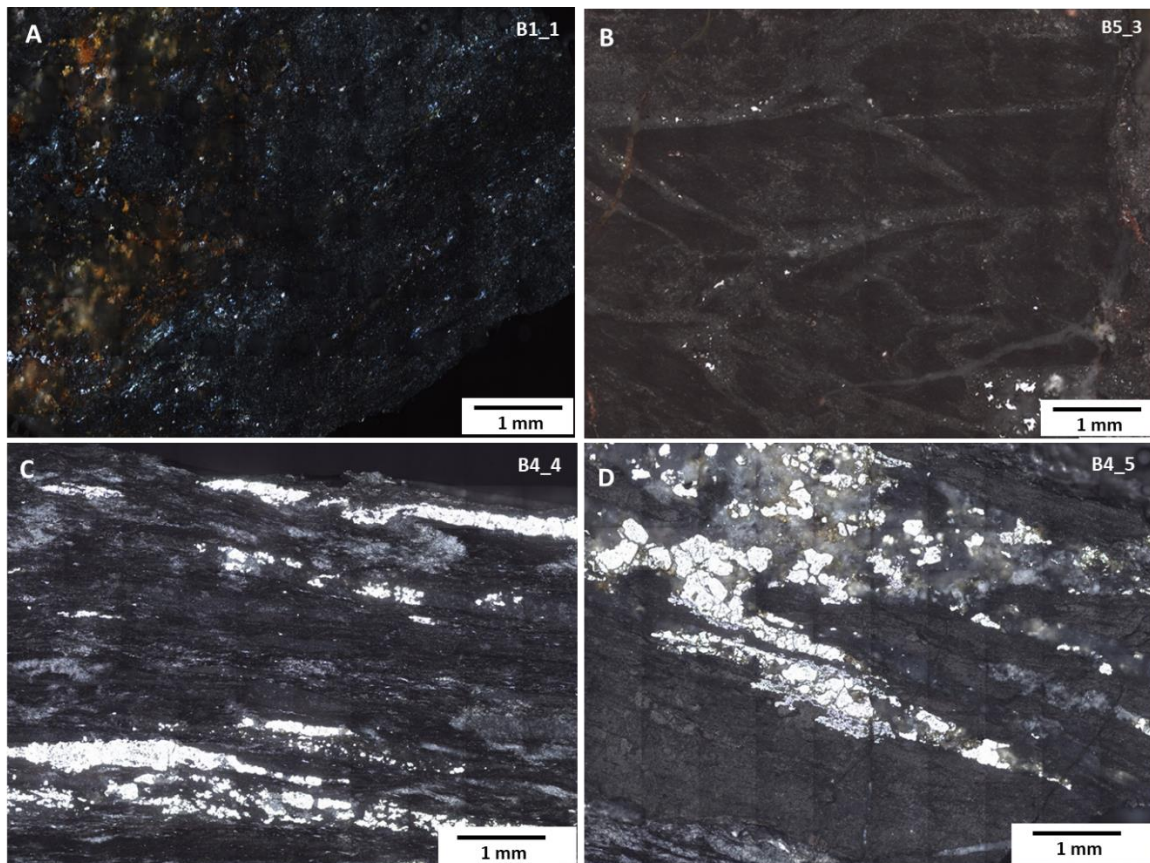


Figure 23 - Mosaics prepared from the assembly of photomicrographs taken from the polished blocks of rock pieces, exhibiting a general petrographic view and main features of samples B1_1, B5_3, B4_4, and B4_5. Photomicrographs taken in reflected white light and 20x immersion oil objective.

3.3.2. Mineralogical analysis

The XRD analysis was done in 4 outcrop samples (ZOM 3, ZOM 8, ZOM 13 and ZOM 10) and in 2 drill core samples (B4_3 and B4_6). The complete results are summarized in the Table 8. The analysis allowed the identification of quartz, plagioclase and muscovite as major mineral phases in all samples, corroborating the petrographic observations, which shows that detrital silicate minerals are the main components.

Chlorite, siderite and rutile are also identified in the analyzed samples. It was also detected arsenopyrite in most of samples (except in sample B4_3), pyrite in the drill core samples and malachite in samples ZOM 3, ZOM 8, ZOM 10 and B4_3.

The SEM-EDX analysis was performed in selected samples (ZOM 3, ZOM 4, ZOM 8, ZOM 10, ZOM 13, B1_3, B2_3, B2_5, B3_2, B4_3, B4_6 and B5_2) to complement petrographic and geochemical data. Most of the minerals identified in XRD analysis were confirmed through SEM-EDX. Aluminosilicates, specifically muscovite (Fig. 24, spectrum Z2; Fig. 25, spectrum Z1), Fe (Fig. 24, spectrum Z1) and Ti oxides (Fig. 24, spectrum Z3; Fig. 26, spectrum Z2) were identified in the studied samples.

Calcium phosphates were detected in samples B1_3, B2_3, B2_6 and B5_2 (Fig. 26, spectra Z1 and Z2). Pyrite was documented in samples B2_3, B2_6, B3_2, B4_3 (framboidal pyrite) and B4_6 (Fig. 25, spectrum Z3; Fig. 27, spectrum Z1), Cu sulfides in sample B2_3 (Fig. 25, spectrum Z2), arsenopyrite and chalcopyrite in sample B3_2 (also in B4_3 and B4_6 samples) associated with quartz (Fig. 27, spectra Z2 and Z4), probably being related to hydrothermal fluids.

Table 8 - Results of the XRD analysis of the studied samples.

Samples	Mineralogy (%)													
	Quartz	Plagioclase	Muscovite	Chlorite	Anhydrite	Pyrite	Arsenopyrite	Galena	Malachite	Azurite	Siderite	Apatite	Monazite	Rutile
ZOM 3	25.0	20.0	23.0	11.0	-	-	3.0	-	2.0	tr	3.0	3.0	-	3.5
ZOM 8	26.5	6.0	17.5	21.5	2.5	-	6.0	-	4.0	tr	2.0	4.0	tr	3.0
ZOM 10	71.0	2.0	6.0	1.0	-	-	8.0	tr	1.0	-	1.0	3.0	tr	tr
ZOM 13	39.5	3.5	32.5	3.5	2.5	-	2.5	-	tr	-	1.5	-	-	7.0
B4_3	62.0	2.5	7.0	3.0	tr	1.0	-	-	2.5	-	12.5	-	-	1.0
B4_6	74.0	3.0	9.5	-	2.5	1.0	tr	-	tr	-	4.5	tr	tr	1.5

tr - traces.

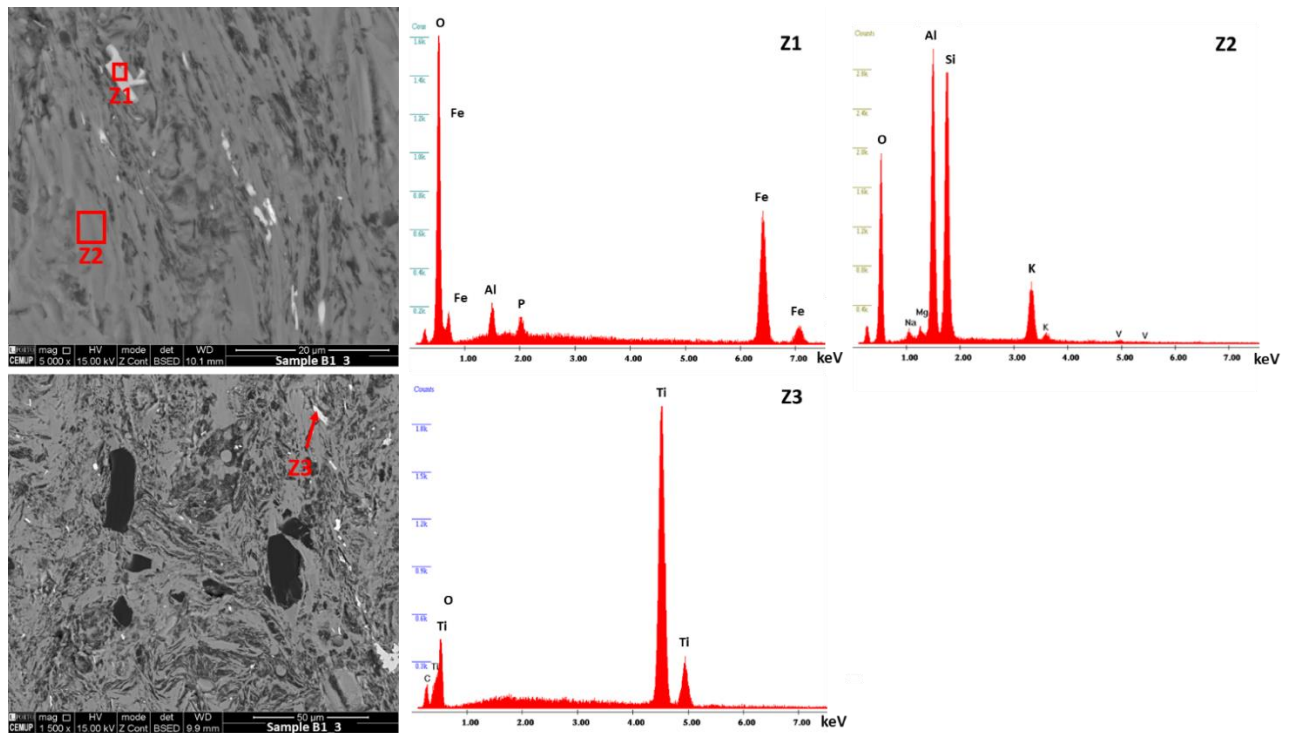


Figure 24 - SEM images and EDX spectra of iron oxides (Z1) and associated aluminosilicates (Z2) and titanium oxides (Z3) interbedded with aluminosilicates in sample B1_3.

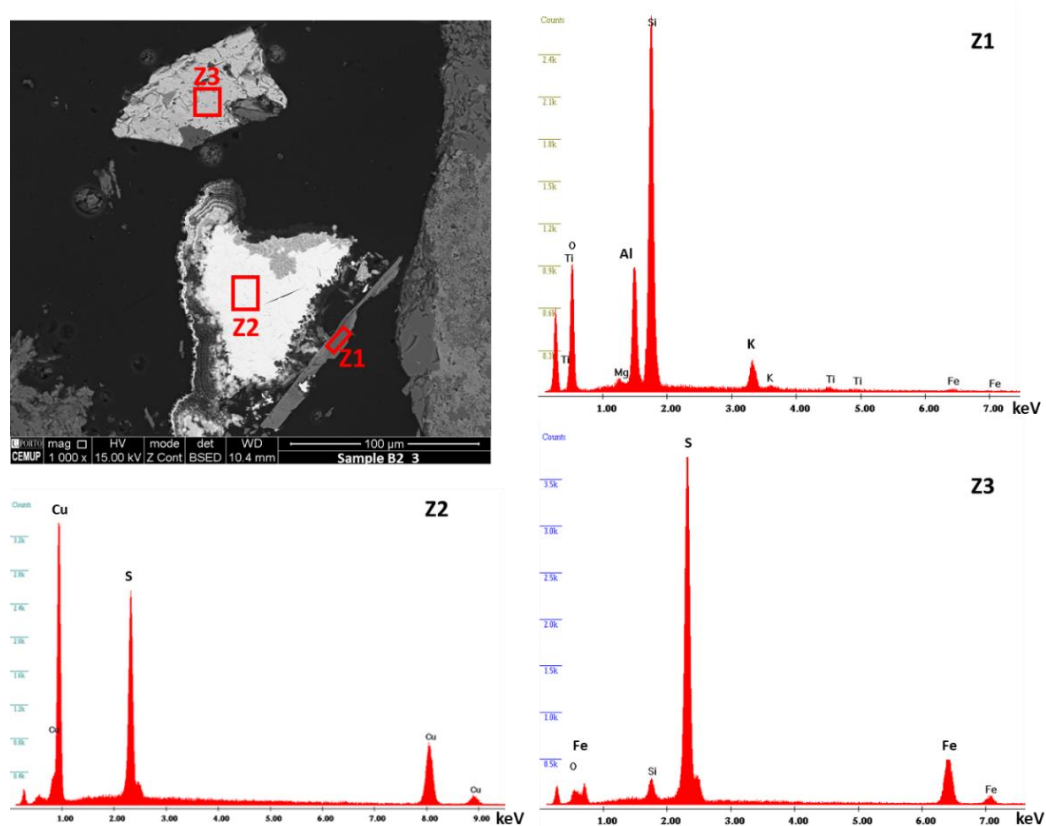


Figure 25 - SEM image and EDX spectra of aluminosilicates (Z1), copper sulfide (Z2) with zonation at the edges of the particle, and iron sulfide (Z3) in sample B2_3.

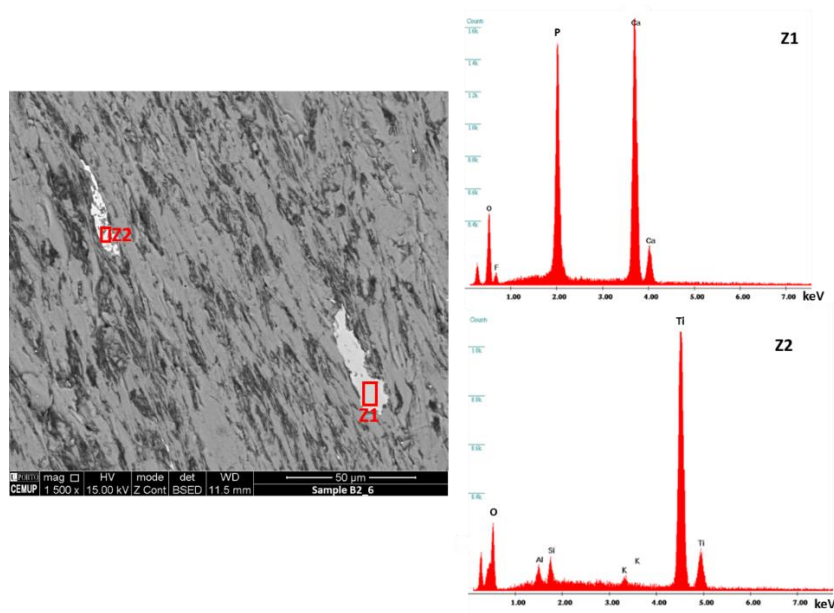


Figure 26 - SEM image and EDX spectra of calcium phosphate (Z1), titanium oxide (Z2), and OM within aluminosilicates in sample B2_6.

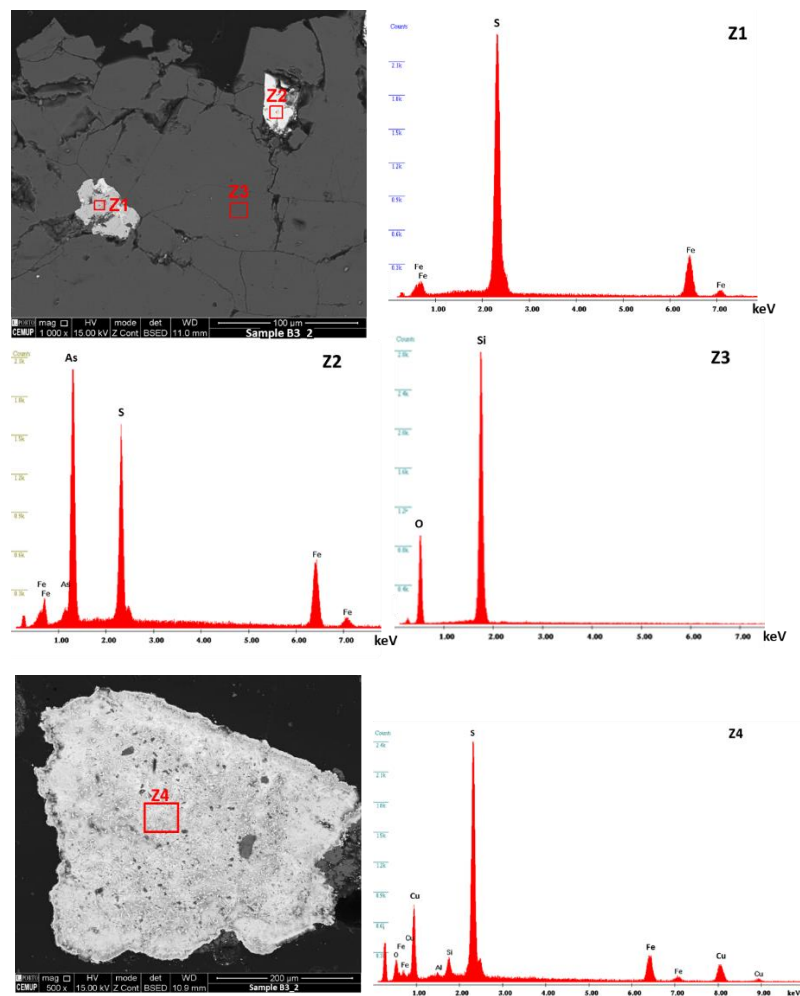


Figure 27 - SEM images and EDX spectra of pyrite (Z1), arsenopyrite (Z2), quartz (Z3), and chalcopyrite (Z4) in sample B3_2.

3.3.3. Reflectance of organic matter

In the absence of vitrinite in the studied samples dated from Silurian, reflectance measurements were carried out in vitrinite-like particles and graptolites. Table 9 resumes the results obtained for reflectance measurements, together with the number of measured particles and standard deviation.

The mean random reflectance of vitrinite-like particles in samples collected near the Alandroal Cu occurrences varies between 3.68% and 4.29%. Far from the mineralization, values of random reflectance of vitrinite-like particles range between 2.99% and 3.64% in Alandroal region, and between 1.93% and 5.36% in Barrancos (Table 9). As respect to the maximum reflectance, values near the Alandroal Cu occurrences varies between 6.48% and 7.67%, and far from Cu occurrences between 5.01% and 6.53% in Alandroal, and between 2.47% and 6.34% in Barrancos region (Table 9). The mean and maximum reflectance (R_r and R_{max}) in Miguel Vacas samples, measure in the vitrinite-like particles, ranges from 1.74% to 4.74% and from 2.27% to 6.66%, respectively.

In samples ZOM 10, ZOM 11, B2_2, B2_3, B3_1, B3_2 and B5_2, the reflectance was also measured in particles of graptolites (R_{grap}) since their occurrence is expressive in these samples and, on the other hand, few vitrinite-like particles were observed. The reflectance of zooclasts, such as graptolites, has been used to determine thermal maturity since reflectance data can be transformed to equivalent vitrinite reflectance values based on empirical correlations (e.g., Bertrand, 1990; Petersen et al., 2013; Hartkopf-Fröder et al., 2015). This means that graptolite reflectance may also be an indicator of thermal maturation of the host rocks (Suárez-Ruiz et al., 2012). The equivalent vitrinite reflectance for the studied samples was calculated (VR_{r-eq} and VR_{max-eq}) according to Petersen et al. (2013) through the equation: $VR_{eq} = 0.73 \times R_{grap} + 0.16$. The values of VR_{r-eq} and VR_{max-eq} range from 3.13% to 4.15% and from 4.86% to 5.31%, respectively in samples from Barrancos; and from 2.57% to 4.53% and from 4.06% to 6.53%, respectively in Miguel Vacas samples. Obtained values are concordant with mean and maximum reflectance values obtained in the other vitrinite-like particles.

Table 9 - Mean (Rr) and maximum reflectance (R_{max}) measured in vitrinite like-particles, equivalent vitrinite mean (VR_{r-eq}) and maximum reflectance (VR_{max-eq}) estimated based on graptolites reflectance, and estimated paleotemperatures based on the random mean reflectance of the studied samples.

	Sample	Depth (m)	Measurements in vitrinite like-particles					Measurements in graptolites					Paleotemperature ² (°C)	
			N	Rr (%)	SD	R _{max} (%)	SD	N (grap)	VR _{r-eq} ¹	SD (grap)	VR _{max-eq} ¹	SD (grap)		
Alandroal	Near mineralization	ZOM 1	-	35	3.92	0.74	6.97	1.51	-	-	-	-	-	327
		ZOM 2	-	47	4.29	1.13	7.08	1.40	-	-	-	-	-	338
		ZOM 3	-	32	4.03	0.62	7.25	1.16	-	-	-	-	-	330
		ZOM 4	-	36	4.09	0.58	7.67	1.24	-	-	-	-	-	332
		ZOM 8	-	32	3.90	0.84	7.12	1.87	-	-	-	-	-	326
		ZOM 9	-	20	3.68	0.80	6.48	1.32	-	-	-	-	-	319
	Far from mineralization	ZOM 13	-	24	2.99	0.74	5.01	1.35	-	-	-	-	-	292
		ZOM 14	-	5	3.64	1.13	6.53	2.76	-	-	-	-	-	317
		ZOM 10	-	12	5.36	0.40	6.34	0.59	52	4.15	0.59	5.31	0.86	334*
Barrancos	ZOM 11	-	11	1.79	0.42	2.47	0.89	12	3.13	1.36	4.86	1.87	298*	
Miguel Vacas	B1	1	25.4	10	2.68	1.18	3.90	2.12	-	-	-	-	-	278
		2*	42.7	8	3.29	0.97	5.67	2.02	-	-	-	-	-	304
		3*	52.1	19	3.55	0.68	4.44	0.88	-	-	-	-	-	314
		4*	55.5	11	3.34	0.74	5.14	1.14	-	-	-	-	-	306
		5	84.0	16	3.31	0.70	5.76	1.35	-	-	-	-	-	305
	B2	1	37.0	21	2.84	0.62	5.08	1.33	-	-	-	-	-	286
		2	46.7	3	4.21	0.49	5.97	0.73	37	4.06	1.64	6.22	1.33	331*
		3	49.9	7	2.91	0.88	4.72	1.07	19	2.57	0.74	4.06	0.93	273*
		4	64.1	15	2.34	0.58	3.20	0.98	-	-	-	-	-	261
		5*	97.1	15	3.09	0.64	3.49	0.84	-	-	-	-	-	296
		6*	127.9	11	1.78	0.49	2.57	0.83	-	-	-	-	-	226
	B3	1	12.4	19	3.21	0.71	4.74	1.17	27	4.16	2.18	5.74	1.73	334*
		2	29.5	14	4.27	0.94	5.34	1.58	27	4.53	1.69	6.53	1.71	345*
		3	55.0	13	3.96	0.99	5.46	1.75	-	-	-	-	-	328
		4*	81.5	15	4.14	1.22	5.42	1.33	-	-	-	-	-	334
		5*	96.6	21	2.75	1.23	3.74	1.06	-	-	-	-	-	282
	B4	1	24.4	14	1.74	0.42	2.43	0.95	-	-	-	-	-	223
		2	43.7	12	2.78	0.46	4.10	1.04	-	-	-	-	-	283
		3	70.4	32	3.80	0.85	4.53	1.08	-	-	-	-	-	323
		4*	130.6	18	2.25	0.57	4.06	1.00	-	-	-	-	-	256
		5*	144.9	10	2.74	0.47	3.79	0.88	-	-	-	-	-	281
		6*	169.7	17	3.30	0.80	4.63	1.14	-	-	-	-	-	305
	B5	1	22.3	4	4.63	0.59	5.92	1.17	-	-	-	-	-	348
		2*	36.3	14	2.85	0.69	4.18	0.73	36	2.96	1.17	4.48	1.28	291*
		3	50.2	18	2.86	0.97	3.67	1.04	-	-	-	-	-	287
		4*	105.0	5	4.74	1.47	5.43	1.67	-	-	-	-	-	351
		5*	119.2	10	2.92	0.73	4.53	1.00	-	-	-	-	-	321
		6*	137.6	9	3.73	0.73	6.66	1.00	-	-	-	-	-	243
		7*	139.9	2	2.04	0.24	2.27	1.16	-	-	-	-	-	289

* samples proximal to mineralized veins; N - number of measured vitrinite like-particles; N_{grap} - number of measured graptolites particles; SD - standard deviation; ¹ VR_{eq} = 0.73 x R_{grap} + 0.16 (Petersen et al., 2013); ² T_{max} = (ln Rr + 1.19)/0.00782 (Barker and Pawlewicz, 1994); * values calculated from equivalent vitrinite reflectance of graptolites.

3.3.4. Geochemical characterization of black shales

The TOC content and the concentration of major, minor and trace elements determined in the studied samples, together with the reference values for black shales (BBS) are presented in Tables 10, 11, and 12.

The results reveal that TOC varies between 0.30% and 15.2% for Alandroal and Barrancos outcrop samples, and between 0.38% and 12.6% for Miguel Vacas samples (Table 11). Table 10 categorizes the analyzed samples according TOC values. Samples with higher TOC are those where the OM is noticeably more abundant under microscopic observations. Most of the samples have TOC values above 3%, samples from Alandroal area generally have low values of TOC, and samples from the drill cores B1 and B5 of Miguel Vacas present significantly lower TOC contents (Table 10).

Table 10 - Total organic carbon of the studied samples.

TOC	Samples
> 10%	ZOM 10 B2_3, B3_1, B4_3, B4_6
10% - 8%	B1_3, B2_4, B3_2, B3_5, B4_1, B4_2
8% - 3%	B1_5, B2_1, B2_2, B4_4, B4_5
3% - 1%	ZOM 11, ZOM 14 B1_1, B1_4, B2_5, B2_6, B3_3, B5_1, B5_2, B5_6, B5_7
< 1%	ZOM 1, ZOM 2, ZOM 3, ZOM 4, ZOM 8, ZOM 9, ZOM 13 B1_2, B3_4, B5_3, B5_4, B5_5

Table 11 - Total organic carbon (TOC, %), concentration of major, minor, and trace elements (ppm) in the studied black shales and reference values for range of BBS (Ketris and Yudovich. 2009).

		Depth (m)	TOC	Al	Ca	Fe	K	Mg wt. %	Na	P	S	Ti	Ag	As	Ba	Be	Bi	Cd	Co	Cr	Cs	Cu	Ga	Hf
																		ppm						
Alandroal (near min.)	ZOM 1	-	0.30	11.1	0.03	4.07	1.79	0.38	1.42	0.06	<0.04	0.39	0.01	17.1	430	4.00	0.09	<0.02	15.6	104	5.40	8.20	34.6	4.66
	ZOM 2	-	0.73	14.8	0.07	0.52	2.80	0.55	0.38	0.02	<0.04	0.77	0.12	3.50	1095	3.00	0.20	<0.02	0.90	80.0	15.2	49.5	32.9	4.44
	ZOM 3	-	0.33	10.6	0.05	3.42	1.90	0.48	1.34	0.03	<0.04	0.58	0.07	25.0	572	5.00	<0.04	0.02	20.7	97.0	8.30	728	31.7	4.07
	ZOM 4	-	0.54	10.2	0.08	3.91	1.94	0.50	0.91	0.04	<0.04	0.33	0.35	20.1	492	3.00	<0.04	<0.02	12.6	92.0	6.70	424	27.3	3.49
	ZOM 8	-	0.35	9.94	0.08	5.54	2.15	0.88	0.57	0.06	<0.04	0.34	0.01	14.6	423	4.00	<0.04	<0.02	40.2	98.0	5.40	32.3	30.0	2.25
	ZOM 9	-	0.43	14.6	0.20	3.36	5.01	1.36	0.11	0.05	<0.04	0.57	0.19	31.8	1591	6.00	<0.04	0.04	4.20	86.0	10.5	13.2	36.6	3.94
Alandroal (far min.)	ZOM 13	-	0.68	10.1	0.03	5.32	2.91	0.40	0.10	0.06	<0.04	0.47	0.19	24.5	937	4.00	0.11	<0.02	1.10	91.0	8.80	17.6	27.7	3.78
	ZOM 14	-	2.14	7.32	0.04	3.22	2.24	0.64	0.13	0.05	<0.04	0.31	0.21	9.30	608	3.00	3.56	<0.02	4.60	178	6.30	118	25.5	3.05
Barrancos (far min.)	ZOM 10	-	15.2	2.73	0.11	0.23	1.10	0.23	0.03	0.02	0.85	0.17	3.87	3.60	171	2.00	0.37	0.45	0.80	47.0	1.00	32.0	14.1	1.11
	ZOM 11	-	2.11	5.96	0.03	0.63	2.56	0.46	0.05	0.02	0.04	0.36	9.62	5.20	416	3.00	0.48	0.10	3.90	187	3.90	198	22.2	3.83
B1	1	25.4	1.14	5.06	0.01	2.97	2.22	0.26	0.17	0.04	<0.04	0.17	0.25	44.5	359	2.00	3.33	<0.02	7.10	67.0	3.20	70.7	16.3	2.01
	2*	42.7	0.38	8.58	0.03	5.74	2.95	0.80	0.32	0.08	<0.04	0.28	0.07	34.9	400	3.00	0.39	<0.02	22.0	82.0	4.40	30.0	26.6	2.03
	3*	52.1	9.10	8.86	0.13	1.37	5.13	0.37	0.39	0.11	<0.04	0.51	0.24	16.2	682	3.00	2.15	<0.02	1.00	331	10.4	185	39.2	4.88
	4*	55.5	2.04	8.48	0.01	2.33	5.01	0.41	0.18	0.06	0.26	0.35	0.65	28.0	370	4.00	3.69	0.08	5.60	130	9.30	1406	30.3	3.43
	5	84.0	3.34	10.1	0.11	0.84	5.90	0.26	0.36	0.07	<0.04	0.49	0.07	15.1	723	4.00	1.68	<0.02	5.10	119	7.20	74.8	38.7	2.99
B2	1	37.0	4.39	7.62	0.14	7.63	1.84	1.57	0.08	0.13	<0.04	0.23	0.25	21.4	301	4.00	2.54	<0.02	13.3	146	2.50	132	25.4	3.94
	2	46.7	5.63	5.50	0.19	4.92	2.52	1.01	0.08	0.08	0.16	0.25	0.38	25.1	410	4.00	0.98	0.36	6.10	168	4.30	60.1	21.7	3.04
	3	49.9	10.4	5.56	1.03	5.71	2.37	0.81	0.07	0.48	4.30	0.21	4.34	10.7	37.0	3.00	3.26	0.08	53.8	265	4.20	775	19.7	2.91
	4	64.1	9.73	5.51	0.36	1.39	3.44	0.59	0.09	0.25	0.74	0.32	0.82	4.70	442	4.00	0.23	0.46	10.5	139	4.90	95.7	23.9	2.63
	5*	97.1	2.56	1.20	0.07	1.64	0.46	0.08	0.02	0.03	1.31	0.04	0.62	52.8	75.0	<1.00	4.85	0.12	5.70	22.0	0.90	30.2	4.36	0.43
	6*	128	2.71	9.53	0.36	0.88	6.36	0.39	0.28	0.09	0.14	0.49	0.11	45.6	686	5.00	0.93	<0.05	5.30	123	6.00	92.3	40.5	4.29
B3	1	12.4	11.7	5.21	0.05	2.82	3.60	0.44	0.06	0.18	2.51	0.32	0.78	11.2	57.0	4.00	0.54	0.22	16.8	190	4.80	58.9	23.7	3.25
	2	29.5	8.74	3.77	0.02	1.53	2.21	0.26	0.03	0.04	1.45	0.20	1.32	207	109	2.00	0.94	0.25	10.2	163	4.80	1455	20.9	2.65
	3	55.0	2.87	7.67	0.45	5.11	4.08	0.44	0.13	0.30	0.09	0.40	0.30	187	563	3.00	0.71	0.20	25.9	160	6.20	1346	26.4	3.67
	4*	81.5	0.90	3.97	0.17	3.28	2.31	0.16	0.06	0.12	0.51	0.13	35.6	388	289	2.00	4.05	0.03	16.7	156	4.40	994	21.8	2.29
	5*	96.6	8.58	3.57	0.26	1.06	2.14	0.11	0.08	0.14	0.15	0.23	6.03	81.8	331	2.00	3.92	<0.02	6.40	179	3.60	467	17.0	2.68
B4	1	24.4	8.41	6.68	0.02	0.42	3.54	0.45	0.07	0.01	<0.04	0.44	0.64	8.50	565	3.00	1.38	<0.02	0.30	141	5.10	27.7	23.9	3.81
	2	43.7	8.11	4.82	1.12	3.32	2.23	0.44	0.05	0.49	2.89	0.21	0.89	43.6	31.0	2.00	0.61	1.91	13.9	136	4.70	207	15.9	2.52
	3	70.4	12.6	4.44	0.58	3.81	2.22	0.55	0.05	0.14	2.26	0.12	1.06	36.1	52.0	3.00	0.44	0.96	11.9	285	4.90	154	18.9	2.30
	4*	131	3.96	8.51	0.36	4.27	3.54	0.63	0.14	0.06	1.72	0.17	0.35	86.0	63.0	3.00	2.32	<0.02	18.4	84.0	7.90	28.2	24.3	3.00
	5*	145	5.76	7.25	1.75	5.02	2.86	1.10	0.12	0.27	2.03	0.25	0.39	89.2	41.0	3.00	3.40	0.02	20.7	148	6.20	80.8	23.2	3.10
	6*	170	11.9	3.95	0.40	1.97	1.73	0.17	0.07	0.18	2.05	0.13	0.45	96.6	94.0	2.00	3.68	0.32	8.10	88.0	3.60	238	14.9	1.82
B5	1	22.3	1.27	4.31	0.01	0.69	2.61	0.37	0.07	0.07	<0.04	0.19	0.67	31.7	390	2.00	3.64	0.15	0.50	152	4.10	30.3	20.2	3.27
	2*	36.3	2.59	4.39	0.01	3.74	2.39	0.30	0.07	0.10	<0.04	0.11	4.07	323	332	4.00	7.65	0.19	3.50	86.0	4.30	129	21.4	2.87
	3	50.2	0.47	2.77	<0.01	3.54	1.44	0.17	0.03	0.03	1.40	0.13	1.31	95.0	212	2.00	1.79	0.23	14.8	139	2.80	149	10.4	1.90
	4*	105	0.43	9.59	2.16	0.80	5.74	0.24	0.26	0.06	<0.04	0.43	0.01	40.4	659	4.00	0.50	<0.02	1.90	90.0	5.30	95.3	38.1	4.31
	5*	119	0.76	8.77	1.26	0.83	4.59	0.36	0.27	0.08	<0.04	0.47	0.19	60.2	457	4.00	4.59	<0.02	4.00	82.0	5.30	219	41.5	3.41
	6*	138	1.63	9.94	0.56	1.00	6.00	0.50	0.33	0.08	<0.04	0.61	0.01	10.5	580	3.00	0.81	<0.02	2.60	102	5.20	12.7	48.9	4.25
	7*	140	1.61	6.77	3.14	1.00	3.36	0.27	0.08	0.04	<0.04	0.35	0.10	39.3	202	3.00	2.42	<0.02	12.9	88.0	3.20	128	24.0	3.41
BBS	min	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	0.93	n.a	1.50	0.40	10.0	270	1.00	0.00	2.00	10.0	50.0	2.00	35.0	9.00	2.50
	max	n.a	n.a	n.a	n.a	n.a	n.a	n.a	n.a	2.20	n.a	4.60	2.40	80.0	800	3.00	4.00	12.0	30.0	160	7.00	150	25.0	6.00

Table 11 - (continuation).

		In	Li	Mn	Mo	Nb	Ni	Pb	Re	Rb	Sb	Sc	Se	Sn	Sr	Ta	Te	Ti	Th	U	Y	V	W	Zn	Zr	REE
		ppm																								
Alandroal (near min.)	ZOM 1	0.12	54.3	251	0.31	14.1	40.5	10.5	0.003	80.4	0.88	16.1	0.15	4.60	92.0	0.90	0.09	0.84	12.5	2.70	6.80	186	1.10	45.9	144	242
	ZOM 2	0.04	8.70	42.0	0.11	21.5	4.00	2.67	<0.002	186	1.78	23.4	0.50	5.10	210	1.80	0.08	2.56	29.7	2.40	14.7	181	3.30	8.40	141	261
	ZOM 3	0.08	67.3	266	0.51	19.8	99.9	3.60	<0.002	89.0	2.51	17.0	0.60	4.80	241	1.40	0.03	1.33	13.4	2.20	8.10	174	1.60	51.9	143	132
	ZOM 4	0.07	50.6	180	0.49	12.9	105	3.36	<0.002	93.2	2.10	16.5	0.40	3.20	222	0.90	0.03	1.47	11.9	2.20	6.40	147	1.00	59.3	109	144
	ZOM 8	0.11	101	108	0.21	11.4	48.3	12.3	<0.002	90.8	0.68	16.4	0.50	3.70	184	0.70	0.06	1.01	10.1	1.70	6.20	135	1.60	109	71.1	115
	ZOM 9	0.11	41.2	36.0	0.08	20.9	30.2	8.82	<0.002	324	2.29	25.8	0.40	5.70	27.0	1.50	0.06	1.13	42.8	3.40	32.3	139	2.60	114	110	663
Alandroal (far min.)	ZOM 13	0.08	13.5	96.0	1.45	16.5	10.2	7.51	<0.002	121	5.35	16.7	1.10	3.90	80.0	1.10	0.03	0.99	15.6	2.60	7.90	148	1.90	25.5	107	180
	ZOM 14	0.05	43.4	440	0.68	11.3	26.4	9.71	0.002	143	3.27	14.8	0.40	3.10	64.0	0.80	0.59	0.79	10.9	3.90	20.2	968	2.60	60.0	126	277
Barrancos (far min.)	ZOM 10	0.01	7.70	23.0	45.5	5.82	27.8	55.0	0.06	39.3	75.5	6.60	22.6	1.10	13.0	0.40	0.20	0.94	3.80	9.90	19.4	773	0.90	45.7	58.3	172
	ZOM 11	0.03	16.4	28.0	1.62	11.4	36.8	71.2	0.05	115	25.9	12.3	1.00	2.40	37.0	0.70	0.23	1.01	8.80	11.5	49.4	1373	1.50	28.8	151	257
B1	1	0.08	28.8	219	3.72	10.0	24.9	10.9	<0.002	106	4.18	10.6	1.5	2.30	40.0	0.70	0.42	0.57	10.3	3.00	8.8	243	0.90	50.8	80.9	131
	2*	0.09	61.0	628	1.18	9.37	76.5	8.28	<0.002	102	2.74	12.6	<0.30	3.40	81.0	0.60	0.11	0.94	8.90	1.40	4.00	124	1.00	111	70.3	90.2
	3*	0.02	11.8	29.0	4.89	17.4	23.1	10.7	0.03	201	6.84	17.7	2.50	4.90	75.0	1.20	0.37	1.52	15.4	13.7	20.2	2454	4.90	13.1	202	242
	4*	0.09	9.00	55.0	10.1	10.4	36.0	9.82	0.12	140	2.65	12.0	29.1	4.10	122	0.60	0.23	1.01	9.80	8.20	11.3	488	4.40	18.6	128	299
	5	0.12	6.50	310	16.0	16.5	25.6	4.54	0.02	210	0.89	16.9	<0.30	6.10	104	1.00	0.34	1.60	11.3	4.50	6.30	295	3.00	14.2	98.2	113
B2	1	0.06	51.3	684	15.6	12.0	68.4	6.93	0.02	32.2	2.83	13.4	1.90	2.60	29.0	0.80	0.29	0.57	6.50	4.50	7.70	329	1.40	97.6	144	112
	2	0.04	30.7	211	59.2	7.88	91.1	16.1	0.11	91.6	8.17	10.3	3.50	2.80	43.0	0.50	0.27	0.87	9.10	6.30	11.6	2011	2.10	53.5	126	149
	3	0.07	26.5	100	23.7	6.29	517	37.2	0.09	101	10.9	11.1	58.8	2.20	91.0	0.40	0.67	0.95	10.4	10.9	23.1	1162	1.30	36.9	126	140
	4	0.05	17.6	80.0	49.8	9.14	99.2	10.7	0.10	119	3.59	12.1	6.50	2.70	82.0	0.60	0.21	1.33	10.4	8.90	14.0	858	2.30	24.6	105	255
	5*	<0.01	3.70	45.0	11.3	1.46	58.5	12.8	0.03	22.9	3.82	2.30	7.80	0.40	12.0	<0.10	0.43	0.20	1.80	2.10	4.30	270	1.80	11.8	19.0	27.5
	6*	0.18	6.00	313	36.1	19.2	49.8	3.40	0.06	207	3.04	20.1	<0.30	13.3	59.0	1.30	0.08	1.29	13.9	12.8	12.4	929	4.70	8.00	165	226
B3	1	0.04	11.6	58.0	44.3	9.38	176	19.1	0.73	137	4.55	14.0	26.5	2.70	547	0.60	0.46	1.46	23.1	20.7	55.1	1935	3.20	34.6	143	526
	2	0.05	5.10	31.0	250	8.08	171	11.9	0.70	106	8.05	10.1	16.8	2.00	105	0.50	0.86	1.12	7.60	16.5	29.6	4025	4.90	12.3	138	251
	3	0.06	11.1	225	19.6	12.3	151	11.7	0.04	147	5.35	15.4	5.70	3.80	74.0	0.70	0.40	1.62	11.4	6.80	16.7	1447	3.70	45.9	138	219
	4*	0.03	4.30	73.0	7.75	5.11	74.9	5.58	0.02	116	3.50	9.20	20.7	5.30	33.0	0.30	0.26	0.75	10.5	8.90	15.8	1655	3.40	21.6	115	702
	5*	0.04	2.00	38.0	4.14	8.65	31.1	4.73	0.01	104	2.47	9.70	5.60	4.30	30.0	0.50	0.22	0.64	6.20	8.20	17.6	2958	2.20	7.40	140	184
B4	1	0.04	14.2	55.0	2.91	13.4	6.90	20.0	0.03	144	4.37	13.3	0.90	3.30	88.0	0.80	0.31	1.22	9.90	6.80	14.5	646	2.70	9.40	141	168
	2	0.04	11.7	269	45.8	5.97	234	17.9	0.09	119	9.09	9.90	24.6	1.80	89.0	0.40	0.31	1.21	8.30	11.6	22.0	2246	1.70	51.0	102	165
	3	0.07	10.8	757	62.2	3.29	132	24.3	0.13	101	7.95	11.9	16.3	1.50	80.0	0.20	0.39	1.17	6.30	14.7	24.4	2197	1.80	71.8	114	306
	4*	0.09	4.90	1076	6.91	5.50	82.7	5.60	0.01	189	2.19	14.3	5.50	3.40	48.0	0.30	0.18	1.42	12.4	5.60	11.0	188	2.90	18.5	105	169
	5*	0.15	10.6	2372	11.2	6.29	120	9.35	0.04	159	3.35	13.9	12.9	4.50	77.0	0.40	0.28	1.23	9.70	11.9	20.5	702	4.90	13.7	130	143
	6*	0.13	5.30	60.0	76.8	4.18	105	11.3	0.16	80.7	2.63	8.40	8.10	3.00	39.0	0.20	0.24	0.67	7.20	10.5	21.7	800	2.60	26.0	80.6	232
B5	1	0.02	10.3	29.0	68.9	5.15	6.20	9.46	0.00	106	7.58	11.0	15.5	2.30	40.0	0.40	0.46	2.26	8.50	9.90	10.3	2422	2.20	6.70	126	118
	2*	0.16	8.90	39.0	43.0	2.40	56.4	11.0	0.04	102	9.74	11.3	26.6	1.90	49.0	0.20	0.50	1.78	8.60	12.7	17.0	503	2.10	25.7	125	145
	3	0.07	3.9	30.0	81.6	4.35	71.1	32.1	0.19	63.5	8.42	7.70	15.4	1.20	39.0	0.30	0.57	0.62	6.20	10.9	34.0	1476	3.20	17.9	89.9	174
	4*	0.09	3.1	257	0.16	17.8	12.5	9.03	<0.002	189	1.21	13.8	<0.30	8.70	115	1.10	0.13	1.62	13.9	2.20	7.40	178	4.00	9.40	133	154
	5*	0.06	4.7	450	0.38	16.0	16.8	4.33	<0.002	126	3.94	11.7	<0.30	5.70	139	1.10	0.16	0.94	12.8	3.00	11.6	231	8.60	7.10	109	450
	6*	0.09	4.6	340	0.54	24.1	14.5	7.29	<0.002	211	1.63	15.2	<0.30	32.3	84.0	1.50	0.10	1.26	18.3	3.40	9.90	187	7.30	9.20	136	301
	7*	0.08	5.6	1150	1.61	13.0	35.2	4.71	<0.002	74.7	2.81	12.1	0.70	4.60	32.0	0.80	0.53	0.41	9.40	3.20	8.20	173	4.90	8.30	113	136
BBS	min	n.a	15.0	200	6.00	7.00	40.0	10.0	n.a	40.0	0.20	7.00	3.00	2.00	100	0.50	1.30	0.50	4.00	4.00	15.0	100	0.00	60.0	60.0	83.8
	max	n.a	50.0	800	60.0	15.0	140	40.0	n.a	120	11.0	20.0	30.0	10.0	300	1.00	3.00	10.0	11.0	25.0	40.0	400	15.0	300	190	197

n.a - data not available; near min - near mineralization; far min - far from mineralization.

From the analyzed major and minor elements, Al, Fe and K are more abundant, followed by minor concentrations of Ca, Mg, Na, P and Ti. This geochemical composition pattern (Table 11) is consistent with the mineralogical constituents identified through microscope observations including detrital minerals, mainly aluminosilicates, quartz, and iron oxides. Sulfur concentration is generally close to the detection limit. However, some samples have S concentration above 1%: B2_3, B2_5, B3_1, B3_2, B4_2, B4_3, B4_4, B4_5, B4_6 and B5_3 (Table 11).

Figure 28 shows the concentration and the distribution pattern of trace elements. The elements with concentration consistently lower than < 1 ppm are Cd, In, Re and Te, whereas Ag, Bi, Mo, Sb, Se, and Ta show concentrations above or below 1 ppm, depending on the group of samples (Fig. 28, Table 11). Relatively to the distribution pattern of the elements in samples from outcrops, some differences are noticed, standing out samples from Alandroal and Barrancos far from mineralization (Fig. 28B); the elements Ag, Pb, Mo, Sb and Se generally have higher concentrations in Barrancos samples (specifically in sample ZOM 10). These elements are known to have affinity with OM (Finkelman, et al., 2018). Otherwise, the sample ZOM 13 reveals lower concentrations of Ag, Cd, Pb, Te and U. Samples from Alandroal region, near to the mineralization (Fig. 28A), reveal higher concentrations of Cu and Mn, being only compared with some values in samples from Miguel Vacas drill cores.

Considering the mean chemical composition of samples from each drill core from Miguel Vacas, it is possible to observe that they have generally a similar pattern (Fig. 28C). However, some differences are noticed and the most relevant are: B3 presents higher concentrations of Ag, As, Cu, Sr and V; B1 shows lower concentrations of Ag, Cd, Mo and Pb (Fig. 28C, Table 11).

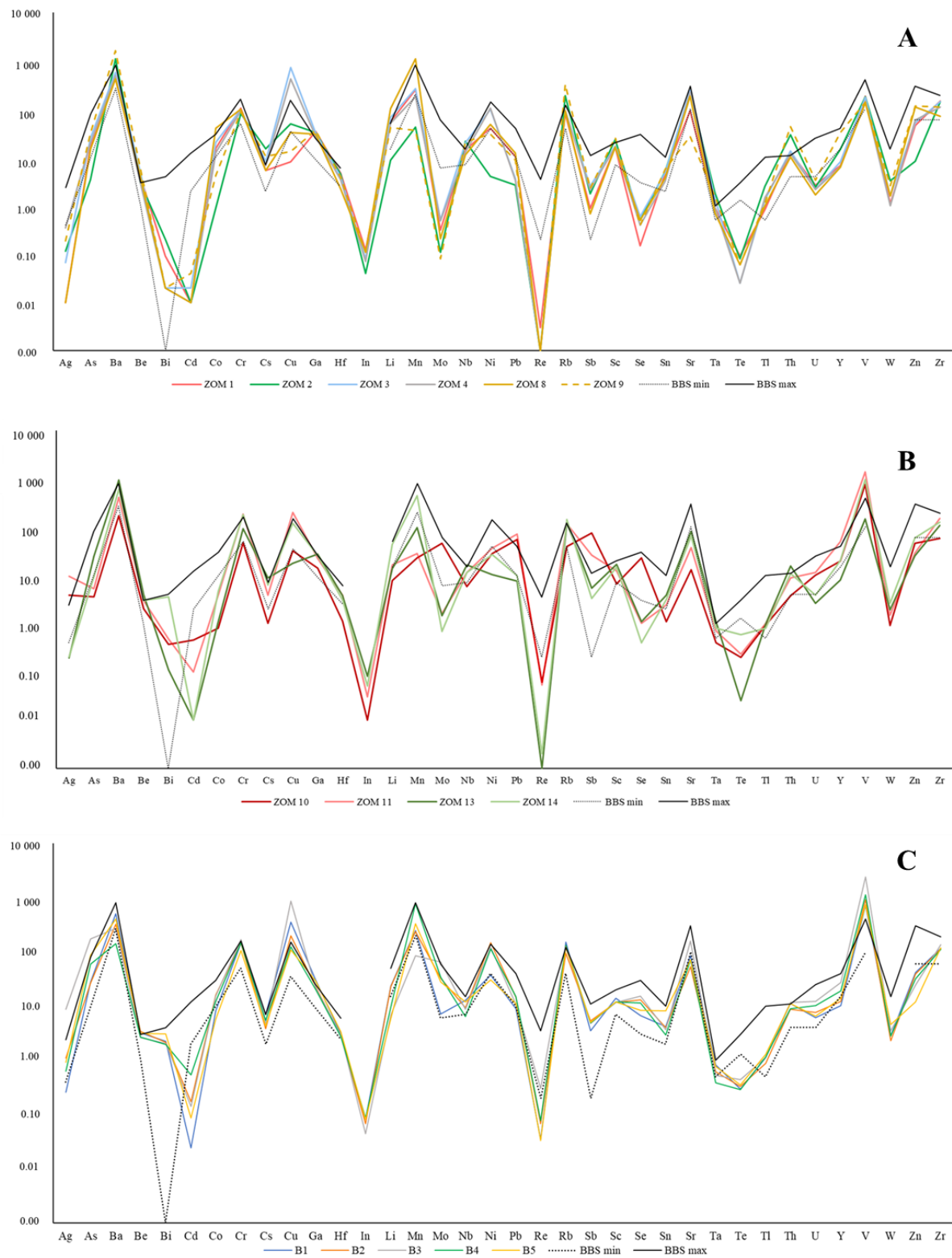


Figure 28 - Concentration of trace elements (ppm) in samples from: A) Alandroal area near to the mineralizations; B) Alandroal and Barrancos area far from mineralization; C) Miguel Vacas area (each line represents the mean chemical composition of samples from each drill core). Range of BBS is also represented.

It is also possible to observe that, in general, the samples from Barrancos and Miguel Vacas with the most depleted profile in REE (Figs. 29 and 30) have in common the fact that are the samples with lower Cu values when compared to the others. In Barrancos, the sample ZOM 10 (Fig. 29B) present a depleted profile and low Cu concentration (32.0 ppm) when compared to the ZOM 11. Samples B1_2, B2_5, B4_4, and B5_1 from Miguel Vacas have Cu concentrations around 30 ppm and have, generally, the most depleted profiles (Fig. 30).

The concentration of rare earth elements (REE) in the studied samples is presented in Table 12. The Σ REE varies from 115 ppm to 663 ppm, with an average value of 244 ppm for the outcrop samples, and from 27.5 ppm to 702 ppm, with an average value of 218 ppm for Miguel Vacas samples (Table 12). The samples from outcrops show consistently higher concentrations of light REE (LREE > 100 ppm) and heavy REE (HREE $\geq$ 10 ppm) compared to drill core samples.

The REE profiles of the black shales samples normalized to BBS (maximum value; Ketris and Yudovich, 2009), presented in the supplementary material (Figs. 29 and 30), are relatively similar, showing lightly flattened profiles. Samples from B3 (Fig. 30C) evidence more differentiated and enriched profiles when compared with the other group of samples, while samples B1_2, B1_5 and B2_5 have a very depleted profile (Fig. 30A and 30B).

All samples have a positive anomaly of Pr and Eu (except sample ZOM 9 and ZOM 14 for Eu). In contrast, the REE profiles show slight negative anomaly of Ce, Nd and Tm. The positive Eu anomaly can be associated with the presence of detrital or hydrothermal plagioclase (Boyong et al., 2011), which is consistent with the XRD analysis.

Table 12 - Concentration of REE (ppm) in the studied black shales and reference values for BBS (Ketris and Yudovich, 2009).

		Depth (m)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣLREE	ΣHREE	REE
Alandroal (near mineralization)	ZOM 1	-	35.9	101	14.5	57.3	13.4	2.60	9.20	0.90	3.70	0.50	1.10	0.20	1.50	0.20	222	19.9	242
	ZOM 2	-	59.5	117	13.5	46.2	8.70	1.70	5.90	0.70	3.00	0.50	1.60	0.30	2.00	0.40	245	16.1	261
	ZOM 3	-	26.1	57.3	7.20	24.4	5.00	1.10	3.30	0.50	2.60	0.50	1.50	0.20	1.60	0.30	120	11.6	132
	ZOM 4	-	26.1	62.0	8.10	29.0	6.10	1.30	4.40	0.50	2.40	0.50	1.30	0.20	1.50	0.30	131	12.4	144
	ZOM 8	-	21.2	49.4	6.40	23.7	4.10	0.90	3.70	0.40	1.80	0.40	1.10	0.20	1.10	0.20	105	9.80	115
	ZOM 9	-	170	297	36.4	112	17.4	2.00	10.4	1.30	5.90	1.10	4.10	0.50	3.30	0.60	634	29.2	663
Alandroal (far from mineralization)	ZOM 13	-	35.7	79.5	9.60	34.7	7.10	1.40	5.10	0.60	2.80	0.40	1.10	0.20	1.40	0.20	167	13.2	180
	ZOM 14	-	60.7	104	15.8	58.8	13.0	2.10	9.00	1.10	5.60	0.90	2.30	0.40	2.50	0.50	252	24.4	277
Barrancos (far from mineralization)	ZOM 10	-	38.8	57.7	10.3	40.5	7.50	1.70	5.40	0.50	3.10	0.70	2.00	0.30	2.60	0.40	155	16.7	172
	ZOM 11	-	59.7	78.1	14.8	57.7	11.4	2.40	9.00	1.30	7.60	1.80	5.40	0.90	5.90	1.10	222	35.4	257
B1	1	25.4	28.5	55.4	6.70	24.8	4.70	1.00	4.00	0.50	2.00	0.40	1.20	0.20	1.50	0.20	120	11.0	131
	2*	42.7	16.1	38.5	4.90	18.8	4.10	1.00	2.80	0.30	1.80	0.20	0.60	0.10	0.90	0.10	82.4	7.80	90.2
	3*	52.1	52.8	87.4	13.8	54.1	10.3	2.00	7.30	0.90	5.00	0.80	2.60	0.40	3.50	0.60	218	23.1	242
	4*	55.5	78.8	127	16.1	53.6	8.20	1.90	4.60	0.50	3.00	0.50	1.60	0.30	2.10	0.30	284	14.8	299
	5	84.0	20.9	46.9	6.20	23.5	5.30	1.00	3.70	0.40	1.90	0.30	0.90	0.10	1.20	0.20	103	9.70	113
B2	1	37.0	19.3	43.6	6.10	24.4	5.20	1.10	4.80	0.50	2.60	0.50	1.50	0.20	1.80	0.30	98.6	13.3	112
	2	46.7	32.3	57.1	8.50	31.6	6.30	1.20	4.60	0.60	2.60	0.40	1.50	0.20	1.90	0.40	136	13.4	149
	3	49.9	28.7	47.2	8.10	31.3	6.20	1.20	5.20	0.70	4.30	0.90	2.60	0.40	2.70	0.50	122	18.5	140
	4	64.1	58.8	93.1	15.0	56.8	11.9	2.20	7.70	0.80	3.80	0.60	1.60	0.30	2.00	0.50	236	19.3	255
	5*	97.1	6.00	10.2	1.30	5.50	1.00	0.40	1.00	0.05	0.80	0.20	0.50	0.05	0.40	0.05	24.0	3.45	27.5
	6*	128	44.9	86.5	12.8	51.6	10.8	2.50	7.50	0.80	3.70	0.60	1.70	0.30	2.30	0.30	207	19.7	226
B3	1	12.4	89.8	163	29.2	124	31.7	9.40	37.6	5.00	23.1	2.90	5.90	0.60	4.00	0.50	437	89.0	526
	2	29.5	51.2	80.4	15.1	61.2	12.1	2.90	11.4	1.40	6.80	1.10	3.10	0.50	3.50	0.60	220	31.3	251
	3	55.0	48.4	77.2	12.3	48.4	10.3	2.30	8.30	1.00	4.50	0.70	2.10	0.30	2.50	0.50	197	22.2	219
	4*	81.5	189	261	41.1	151	25.4	6.70	15.8	1.40	5.40	0.50	1.60	0.30	2.20	0.40	668	34.3	702
	5*	96.6	43.6	60.6	10.7	42.1	8.10	1.80	6.40	0.70	3.70	0.60	2.00	0.30	2.70	0.50	165	18.7	184
B4	1	24.4	34.3	65.1	9.70	37.0	6.20	1.40	4.90	0.60	3.10	0.60	2.00	0.30	2.50	0.50	152	15.9	168
	2	43.7	36.5	57.1	9.50	36.5	6.60	1.80	5.80	0.80	4.30	0.90	2.20	0.40	2.30	0.40	146	18.9	165
	3	70.4	78.1	88.7	20.4	78.3	14.1	2.40	9.70	1.00	5.20	1.00	2.80	0.40	3.10	0.60	280	26.2	306
	4*	131	34.5	74.9	9.40	31.8	6.30	1.40	3.70	0.50	2.60	0.40	1.10	0.30	1.40	0.30	157	11.7	169
	5*	145	30.2	53.7	7.90	28.4	6.00	1.90	4.60	0.70	3.50	0.70	2.10	0.40	2.90	0.40	126	17.2	143
	6*	170	56.5	75.3	14.7	54.5	9.80	2.50	7.10	0.70	4.20	0.70	3.30	0.30	2.40	0.40	211	21.6	232
B5	1	22.3	26.2	42.3	7.20	27.3	4.60	1.10	3.10	0.40	1.60	0.40	1.20	0.20	1.90	0.40	108	10.3	118
	2*	36.3	34.2	52.8	8.30	31.2	5.50	1.30	3.40	0.40	2.80	0.50	1.90	0.30	2.30	0.50	132	13.4	145
	3	50.2	38.5	50.0	10.0	39.9	8.70	1.90	7.90	1.10	6.30	1.20	3.70	0.50	3.90	0.60	147	27.1	174
	4*	105	29.5	63.6	8.60	34.0	6.40	1.40	4.30	0.40	1.90	0.30	1.10	0.20	1.50	0.30	142	11.4	154
	5*	119	112	205	24.0	80.1	12.4	2.70	6.20	0.80	3.40	0.50	1.60	0.20	1.50	0.30	433	17.2	450
	6*	138	64.6	136	16.8	56.3	10.2	3.00	6.40	0.70	3.20	0.40	1.40	0.30	1.90	0.30	284	17.6	301
	7*	140	27.7	55.7	7.50	27.1	5.90	1.30	4.40	0.50	2.10	0.40	1.10	0.20	1.70	0.30	124	12.0	136
BBS	min	-	20.0	35.0	2.50	15.0	2.50	1.00	2.50	0.50	1.00	0.20	1.00	0.30	2.00	0.30	75.0	8.80	83.8
	max	-	40.0	80.0	6.00	45.0	7.00	1.40	6.00	0.90	4.00	0.60	2.00	0.55	3.50	0.45	178	19.4	197

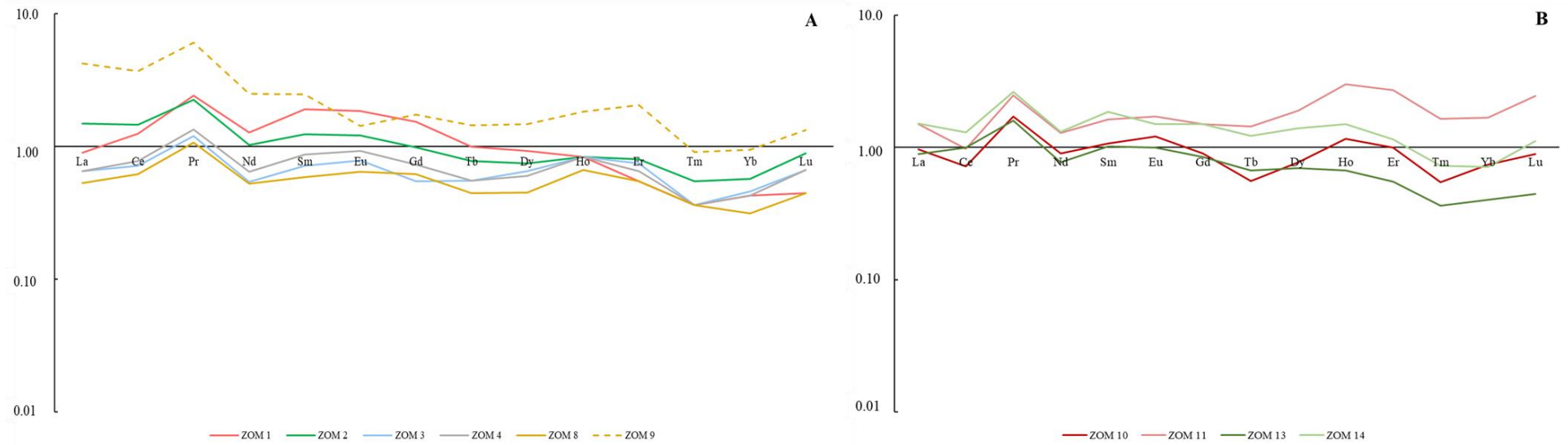


Figure 29 - BBS-normalized REE patterns for the studied samples from: A) Alandroal area near mineralizations and B) Alandroal and Barrancos area far from mineralizations.

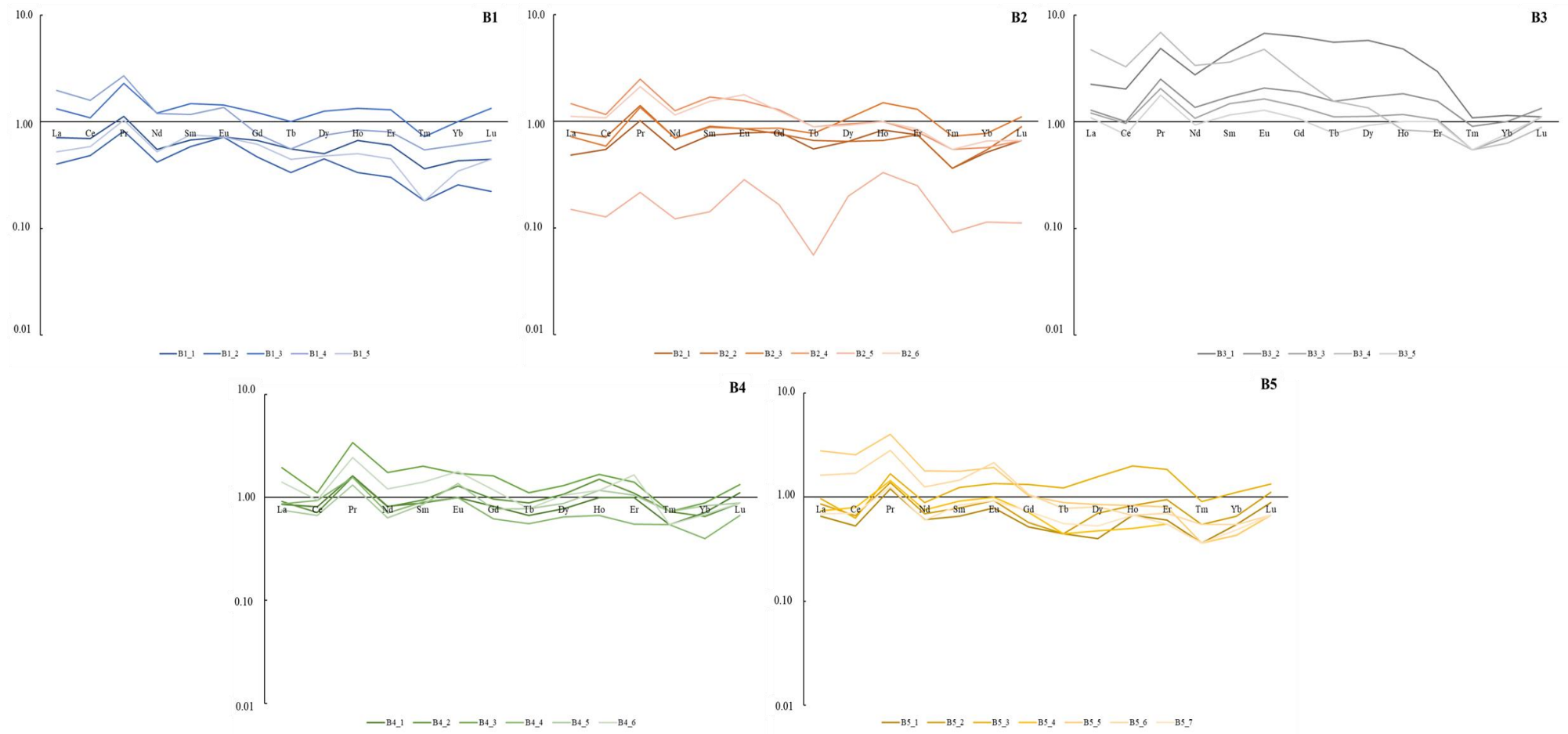


Figure 30 - BBS-normalized REE patterns for the studied samples from drill cores in Miguel Vacas.

3.4. Discussion

3.4.1. Maturation and paleotemperature

The maturation of dispersed OM in rocks is a process that affects the OM after its deposition, resulting from the burial history and being controlled by an increase and duration of heating and pressure (Suárez-Ruiz et al., 2012). To evaluate the maturation of the OM, the classification proposed by Kwiecinska and Petersen (2004) based on the $R_{\max}$ values was considered. The OM in the studied samples can be classified between the rank stage of anthracite, when $2.0\% < R_{\max} < 5.0\%$, and meta-anthracite, when $R_{\max}$ ranges from 5.0% to 6.5%. Anthracite and meta-anthracite are natural precursors of semi-graphite when OM is subjected to high geothermal gradient, and/or to high pressure and/or tectonic stress. Anthracite, meta-anthracite, and semi-graphite are transitional phases of graphite that represent varying degrees of graphitization of carbon contained in the OM with growing molecular structure order (Li et al., 2022).

Figure 31 presents the determined mean and maximum reflectance values, as well as the fields for anthracite, meta-anthracite and semi-graphite classification. Samples from Alandroal area (near the mineralization), with the exception of ZOM 9, correspond to semi-graphite stage with $R_{\max} > 6.5\%$ (Fig. 31A). The OM in samples far from the mineralization (including from Alandroal and Barrancos) have a maturation range between meta-anthracite (ZOM 13, ZOM 11 and ZOM 10) and semi-graphite (ZOM 14) (Fig. 31A). Generally, samples near mineralization present higher OM maturation, possibly resulting from thermal maturation associated to hydrothermal fluids.

As respect to the samples from the drill cores (Figs. 31B to 31F), the maturation of OM varies between the range of anthracite and semigraphite, although most of samples show a thermal maturation compatible with the anthracite rank. Only samples B3_2 and B5_5 have $R_{\max}$ higher than 6.5%, thus in the semi-graphite field (Figs. 31D and 31F), and therefore higher maturation. Samples from B2, B3 and B5 do not exhibit variable maturation of OM with depth, presenting a heterogeneous pattern, while in drill cores B1 and B4, the maturation seems to show an increase trend with depth (Figs. 31 and 32).

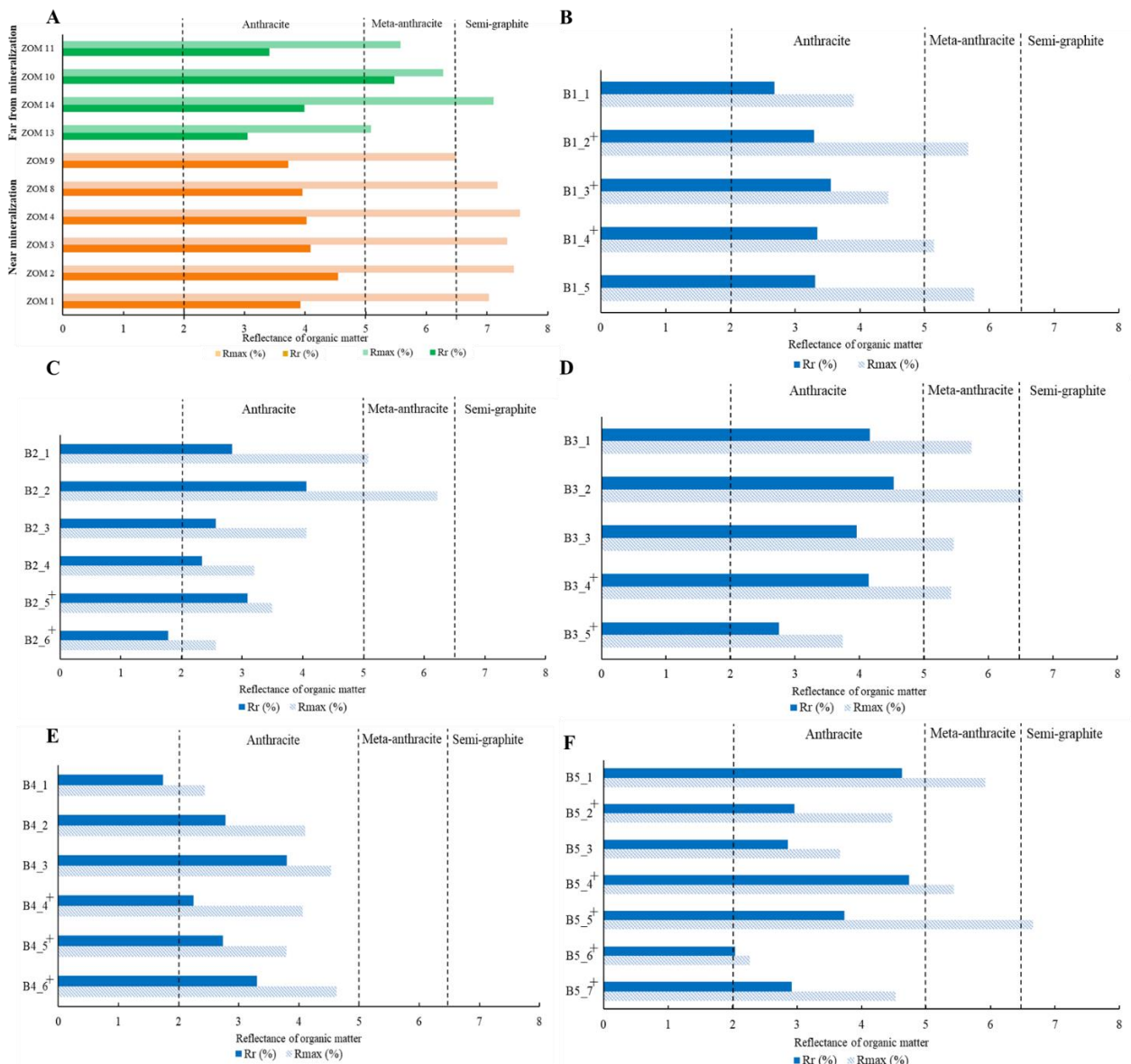


Figure 31 - Mean and maximum reflectance of OM in: A) samples near and far from the mineralizations, from Alandroal and Barrancos area; B) samples from B1; C) samples from B2; D) samples from B3; E) samples from B4; F) samples from B5. Fields anthracite, meta-anthracite and semi-graphite based on $R_{\max}$ values.

The reflectance of OM can also be used to estimate paleotemperatures associated with the maturation and discuss processes that condition it, as for example, tectono-metamorphic activity, circulation of hydrothermal fluids or magmatic intrusions (e.g., Eakin and Gize, 1992; Landais, 1993). The estimation of paleotemperatures based on reflectance of OM can be made using Barker and Pawlewicz (1994) equation: $T_{\max} = (\ln R_r + 1.19)/0.00782$, being R_r the vitrinite random reflectance. This equation considers that the hydrothermal metamorphism includes hydrothermal ore deposits and active geothermal systems.

The maximum temperatures estimated for the studied samples are presented in Table 9, and were calculated considering the random reflectance of vitrinite-like particles for the majority of samples and the random equivalent vitrinite reflectance in samples ZOM 10, ZOM 11, B2_2, B2_3, B3_1, B3_2 and B5_2.

Generally, outcrop samples show higher values of paleotemperatures ($> 300^{\circ}\text{C}$) than the drill core samples from Miguel Vacas. The paleotemperatures vary between 319°C and 338°C in Alandroal area near to the mineralizations, between 292°C and 317°C in Alandroal area far to mineralization, and between 298°C and 334°C in Barrancos area (Table 9). In Miguel Vacas samples the value of paleotemperatures range from 223°C to 351°C (Table 9).

The irregular profiles of maturation with depth in the Miguel Vacas drill cores, often with lower mean random reflectance values (R_r) underlying higher values of reflectance of OM (Fig. 32), could be related to the circulation of hydrothermal fluids. Indeed, some authors (e.g., Barker, 1991; Glikson et al., 2000) concluded that these irregular profiles are a characteristic feature of OM that matured through fast heating due to irregular heat distribution in hydrothermal-geothermal systems. The higher values of mean random reflectance were detected at variable depths, an even at different levels within drill cores B2, B3, and B5, displaying a vertical and lateral variation on the reflectance of OM. This supports that the maturation resulted probably from the circulation of hydrothermal fluids related with Cu-ore deposit genesis. The localized higher values of paleotemperatures in some samples may indicate the proximity to the mineralized vein or local veining (Table 9; Fig. 32).

The higher values of reflectance of the outcrop samples ZOM 2, ZOM 3 and ZOM 4 could be explained by the proximity to Mociços Cu vein deposit (Fig. 13A). However, sample ZOM 1, located 1 km to SW (Fig. 13A) show similar values of reflectance, which can indicate a more regional pattern of fluid circulation. Nevertheless, the discrepant maturation associated with hydrothermal evolution of Cu-ore deposits do not explain all the pattern, and a regional model should be considered (see section 3.4.5).

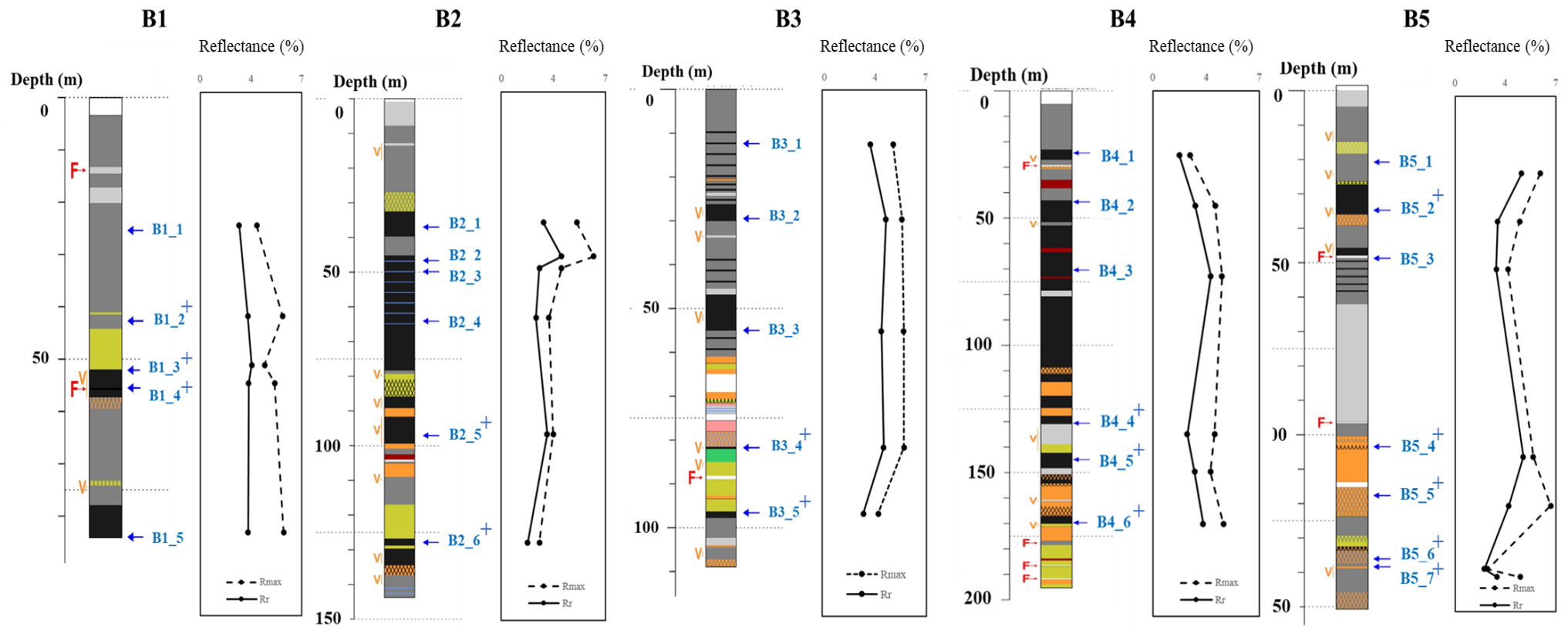


Figure 32 - Maturation profiles in Miguel Vacas.

3.4.2. Elements enrichment and mode of occurrence

The concentration coefficients (CC) were calculated in order to compare the geochemical composition of samples with standard values, namely the BBS (Ketris and Yudovich, 2009). The CC were calculated through the ratio between elements concentration in the studied samples and their concentration in reference data and provides information about the depletion ($CC < 1$) or enrichment ($CC > 1$) of elements comparatively with BBS. The CC were determined considering the maximum reported values for BBS. The CC of REE were estimated considering the sum of LREE and HREE. Table 13 shows the group of elements classified according with Dai et al. (2015, 2016): significant enriched $CC > 10$; slightly enriched $2 < CC < 10$, normal $1 < CC < 2$; and depleted $CC < 0.5$.

Most elements are depleted or have concentrations close to the values reported for BBS, this is, concentrations identified as normal ($CC < 1$) to slightly enriched ($1 < CC < 2$) (Table 13), both in the outcrop samples and in the drill core samples. As respect to the outcrop samples, the majority of the samples shows normal to slightly enriched concentrations of most elements. Exception to Barrancos samples, which are slightly enriched in Sb and Ag, mainly in sample ZOM 11 (Table 13). In Alandroal region, it should be highlighted the enrichment of Cu ($2 < CC < 10$) in two samples collected near the Mociços Cu deposit (ZOM 3 and ZOM 4). The presence of Cu secondary phases (malachite) as trace mineral in ZOM 3 was identified XRD studies, which can explain the enrichment in Cu in those samples. Other elements as Th, Rb, V, REE, Li, Be, and Cs are occasionally enriched in some outcrop samples ($2 < CC < 10$).

As respect to Miguel Vacas drill cores, the enrichment of Ag, As, Cu, V, and REE is noticeable in several samples, namely in black shales from B3, featuring $CC > 10$ for Ag and V (Table 13). The drill core B3 shows significant enrichment in Cu in all samples with exception to the most superficial one. It should be emphasized that is a transversal behavior in the most superficial samples of all drill cores. The elements Cr, Ni, Th, Mo, Mn and Sn are also occasionally enriched in some drill core samples ($2 < CC < 10$).

Table 13 - Concentration coefficients (CC > 1) of trace elements in the studied samples relatively to BBS. Samples proximal to mineralized veins are marked in bold and with the symbol +.

	Samples	1 < CC < 2	2 < CC < 10	CC > 10
Alandroal near mineralization	ZOM 1	Be, Ga, Li, Th, LREE	-	-
	ZOM 2	Ba, Be, Ga, Nb, Rb, Sc, Ta, LREE	Cs, Th	-
	ZOM 3	Be, Cs, Ga, Li, Nb, Ta, Th	Cu	-
	ZOM 4	Be, Ga, Li, Th	Cu	-
	ZOM 8	Be, Co, Ga, Mn	Li	-
	ZOM 9	Ba, Cs, Ga, Nb, Sc, Ta, HREE	Be, Rb, Th, LREE	-
Alandroal far from mineralization	ZOM 13	Ba, Be, Cs, Ga, Nb, Rb, Ta, Th, LREE	-	-
	ZOM 14	Be, Cr, Ga, Rb, LREE, HREE	V	-
Barrancos far from mineralization	ZOM 10	Ag, Pb, V, LREE	Sb	-
	ZOM 11	Be, Cr, Cu, Pb, Y, LREE	Ag, Sb, V, HREE	-
Miguel Vacas B1	1	-	-	-
	2⁺	Be, Ga, Li	-	-
	3⁺	Be, Cs, Cu, Ga, Nb, Rb, Ta, Th, Zr, LREE, HREE	Cr, V	-
	4⁺	Be, Cs, Ga, Rb, V, LREE	Cu	-
	5	Be, Cs, Ga, Nb, Rb, Ta, Th	-	-
Miguel Vacas B2	1	Be, Ga, Li	-	-
	2	Be, Cr	V	-
	3	Ag, Be, Co, Cr, Se, HREE	Cu, Ni, V	-
	4	Be, LREE	V	-
	5⁺	Bi	-	-
	6⁺	Be, Ga, Nb, Rb, Sc, Sn, Ta, Th, LREE	V	-
Miguel Vacas B3	1	Be, Cr, Ni, Rb, Sr, Y	Th, V, LREE, HREE	-
	2	Cr, Ni, LREE, HREE	As, Cu, Mo	V
	3	Be, Cr, Ga, Ni, Rb, Th, LREE, HREE	As, Cu, V	-
	4⁺	Bi, HREE	As, Cu, V, LREE	Ag
	5⁺	As, Cr, LREE	Ag, Cu, V	-
Miguel Vacas B4	1	Be, Rb, V	-	-
	2	Cu, Ni, HREE	V	-
	3	Be, Cr, Cu, Mo, HREE	V, LREE	-
	4⁺	As, Be, Cs, Mn, Rb, Th	-	-
	5⁺	As, Be, Rb, V	Mn	-
	6⁺	As, Cu, Mo, LREE, HREE	V	-
Miguel Vacas B5	1	Mo	V	-
	2⁺	Ag, Be, Bi, V	As	-
	3	As, Mo, LREE, HREE	V	-
	4⁺	Be, Ga, Nb, Rb, Ta, Th	-	-
	5⁺	Be, Bi, Cu, Ga, Nb, Rb, Ta, Th	LREE	-
	6⁺	Be, Ga, Nb, Rb, Ta, Th, LREE	Sn	-
	7⁺	Be, Mn	-	-

To understand the elements mode of occurrence of Alandroal (near mineralization) and Miguel Vacas samples, the Pearson correlation coefficients were calculated, and particular consideration was given to slightly enriched elements ($2 < CC < 10$). The samples far from mineralization and Barrancos were not included, since they present discrepant values in comparison with the remaining outcrop samples. Table 14 shows the Pearson correlation coefficients for selected elements and positive correlations significant at $p < 0.05$ are identified in blue at, while negative correlations significant at $p < 0.05$ are marked in red.

Table 14 - Pearson correlation coefficients between selected elements.

	TOC	Al	Fe	K	P	S	Ti	Ag	As	Co	Cr	Cs	Cu	Mo	Nb	Ni	Pb	Sb	Sc	Th	U
TOC																					
Al	-0.47																				
Fe	-0.03	-0.01																			
K	-0.12	0.51	-0.41																		
P	0.53	-0.26	0.32	-0.08																	
S	0.65	-0.45	0.24	-0.31	0.70																
Ti	-0.30	0.86	-0.35	0.63	-0.24	-0.47															
Ag	-0.06	-0.27	0.05	-0.16	0.08	0.04	-0.28														
As	-0.08	-0.39	0.10	-0.19	0.04	0.00	-0.42	0.70													
Co	0.10	-0.05	0.68	-0.32	0.52	0.51	-0.22	0.11	0.02												
Cr	0.65	-0.22	0.12	0.07	0.43	0.38	-0.09	0.13	-0.03	0.21											
Cs	-0.17	0.78	-0.18	0.42	-0.16	-0.23	0.74	-0.13	-0.19	-0.17	0.07										
Cu	0.07	-0.15	0.09	-0.04	0.19	0.11	-0.09	0.34	0.45	0.26	0.23	0.09									
Mo	0.41	-0.47	-0.09	-0.23	0.05	0.33	-0.38	-0.04	0.30	-0.05	0.22	-0.23	0.36								
Nb	-0.38	0.84	-0.32	0.66	-0.31	-0.54	0.95	-0.26	-0.41	-0.25	-0.14	0.59	-0.11	-0.38							
Ni	0.50	-0.29	0.44	-0.27	0.78	0.83	-0.32	0.07	0.04	0.73	0.43	-0.19	0.35	0.27	-0.37						
Pb	0.47	-0.46	0.28	-0.30	0.45	0.68	-0.41	-0.05	-0.08	0.44	0.49	-0.33	0.04	0.29	-0.46	0.64					
Sb	0.43	-0.58	0.16	-0.29	0.46	0.51	-0.47	0.05	0.27	0.15	0.54	-0.27	0.20	0.52	-0.54	0.56	0.69				
Sc	-0.26	0.91	-0.03	0.54	-0.18	-0.36	0.81	-0.23	-0.30	-0.06	0.00	0.80	-0.15	-0.32	0.78	-0.21	-0.37	-0.41			
Th	-0.20	0.72	-0.14	0.45	-0.14	-0.17	0.69	-0.09	-0.20	-0.16	-0.09	0.70	-0.17	-0.25	0.64	-0.15	-0.21	-0.28	0.80		
U	0.71	-0.50	-0.06	-0.01	0.41	0.57	-0.35	0.13	0.28	0.02	0.65	-0.11	0.22	0.60	-0.42	0.41	0.45	0.62	-0.20	-0.12	
V	0.58	-0.54	-0.12	-0.17	0.29	0.33	-0.34	0.20	0.27	-0.05	0.66	-0.17	0.38	0.69	-0.37	0.29	0.32	0.61	-0.31	-0.24	0.73

The results reveal a significant positive correlation coefficient between TOC and S, Cr and U ($r \geq 0.65$, $p < 0.05$; Table 14) and a positive association with Mo, Ni, Pb, Sb and V ($r > 0.40$, $p < 0.05$; Table 14), which is an organic elemental association generally reported in several studies (Swaine, 1990; Liu et al., 2015; Finkelman et al., 2018; Laranjeira et al., 2023a).

The positive correlation between TOC and S ($r = 0.65$, $p < 0.05$; Table 14) indicates the occurrence of sulfides in association with OM, which corroborates the petrographic and SEM-EDX analysis. The strong positive correlation between S and Ni ($r = 0.83$, $p < 0.05$; Table 14), between S and Pb ($r = 0.68$, $p < 0.05$), and weak positive association with other metals such as Fe, Co, Cr, Cu, Pb and Sb indicate that S is partially inorganically bound.

Other elements have a negative correlation with TOC and a positive correlation with Al, pointing out their association with aluminosilicates (El-Answar et al., 2018; Finkelman et al., 2018; Laranjeira et al., 2023a). These include the elements Ti ($r = 0.86$, $p < 0.05$), Cs ($r = 0.78$, $p < 0.05$), Nb ($r = 0.84$, $p < 0.05$), Sc ($r = 0.91$, $p < 0.05$), and Th ($r = 0.72$, $p < 0.05$).

3.4.3. Redox sensitive elements and paleo-redox conditions

The paleodepositional environments include oxic, suboxic or anoxic conditions. Anoxic conditions may be non-sulfidic or sulfidic; in the latter case, they are also designated euxinic when H_2S occurs within the water column. Suboxic environments are characterized by extremely low but generally nonzero O_2 concentrations in the water column, where H_2S is limited to pore waters below the sediment-water interface. Under oxic conditions, aerobic organisms can use dissolved O_2 from the overlying and interstitial waters for their metabolism. As dissolved O_2 becomes depleted, the OM decomposition continues via organisms using secondary oxidant sources: nitrate, manganese oxides and iron oxides, oxyhydroxides, and sulfate (Tribovillard et al., 2006).

Some trace elements, such as Cd, Co, Cr, Mo, Ni, Th, U, and V, are sensitive to variations of oxygenation conditions during deposition. Some ratios (e.g., Ni/Co, V/Cr and Th/U) have been widely used as an indicator for understanding the paleo-redox conditions during deposition processes (e.g., Hatch and Leventhal, 1992; Jones and Manning, 1994; Rimmer, 2004; Tribovillard, 2006, Ross and Bustin, 2009). These ratios should be used with some caution and critically when studying material that may be affected by weathering due to the sensitivity of some of these elements.

The ratios Ni/Co, V/Cr and Th/U were calculated for the studied samples (Table 15). Higher values of the ratio Ni/Co are related to progressively lacking O_2 during the deposition of the sediments (Jones and Manning, 1994), due to the relative facility of Ni to concentrate in sediments deposited under reducing conditions (e.g., Shaw et al., 1990; Emerson and Huested, 1991; Jones and Manning, 1994). In turn, Co concentration is considered to depend on detrital content, and not influenced by redox conditions (Dill, 1986; Ross and Bustin, 2006). Therefore, higher values of Ni/Co ratio (> 7) indicates anoxic conditions, while lower values (< 5) indicates oxic conditions (e.g., Galarraga et al., 2008; Pi et al., 2014; Eric et al., 2019). Other authors also suggested that V is more concentrated in sediments deposited under reducing conditions (e.g., Shaw et al., 1990; Emerson and Huested, 1991; Jones and Manning, 1994), being considered that V/Cr

ratio above 2 indicate anoxic depositional conditions, while values below 2 are indicative of an oxic environment (Jones and Manning, 1994).

Table 15 - Ratio of selected redox sensitive elements for the studied samples (values corresponding to anoxic depositional conditions in bold).

	Samples	Ni/Co	V/Cr	Th/U
Alandroal Near mineralization	ZOM 1	2.60	1.79	4.63
	ZOM 2	4.44	2.26	12.4
	ZOM 3	4.83	1.79	6.09
	ZOM 4	8.32	1.60	5.41
	ZOM 8	1.20	1.38	5.94
	ZOM 9	7.19	1.62	12.6
Alandroal Far from mineralization	ZOM 13	9.27	1.63	6.00
	ZOM 14	5.74	5.44	2.79
Barrancos Far from mineralization	ZOM 10	34.8	16.5	0.38
	ZOM 11	9.44	7.34	0.77
Miguel Vacas B1	1	3.51	3.63	3.43
	2	3.48	1.51	6.36
	3⁺	23.1	7.41	1.12
	4⁺	6.43	3.75	1.20
	5 ⁺	5.02	2.48	2.51
Miguel Vacas B2	1	5.14	2.25	1.44
	2	14.9	11.9	1.44
	3	9.60	4.38	0.95
	4	9.45	6.17	1.17
	5 ⁺	10.3	12.3	0.86
	6 ⁺	9.40	7.55	1.09
Miguel Vacas B3	1	10.5	10.2	1.12
	2	16.8	24.7	0.46
	3	5.81	9.04	1.68
	4 ⁺	4.49	10.6	1.18
	5 ⁺	4.86	16.5	0.76
Miguel Vacas B4	1	23.0	4.58	1.46
	2	16.8	16.5	0.72
	3	11.1	7.71	0.43
	4 ⁺	4.49	2.24	2.21
	5 ⁺	5.79	4.74	0.82
	6 ⁺	13.0	9.09	0.69
Miguel Vacas B5	1	12.4	15.9	0.86
	2 ⁺	16.1	5.85	0.68
	3	4.80	10.6	0.57
	4 ⁺	6.58	1.98	6.32
	5 ⁺	4.20	2.82	4.27
	6 ⁺	5.58	1.83	5.38
	7 ⁺	2.73	1.97	2.94

The higher Ni/Co and V/Cr are found in the samples ZOM 10, ZOM 11, B1_3, B1_4, all samples from B2 (with exception of B2_1), B3_1, B3_2, all samples from B4 (except B4_4 and B4_5), B5_1 and B5_2, which suggest more anoxic conditions during deposition (Fig. 33). These samples, generally, are those with higher TOC values.

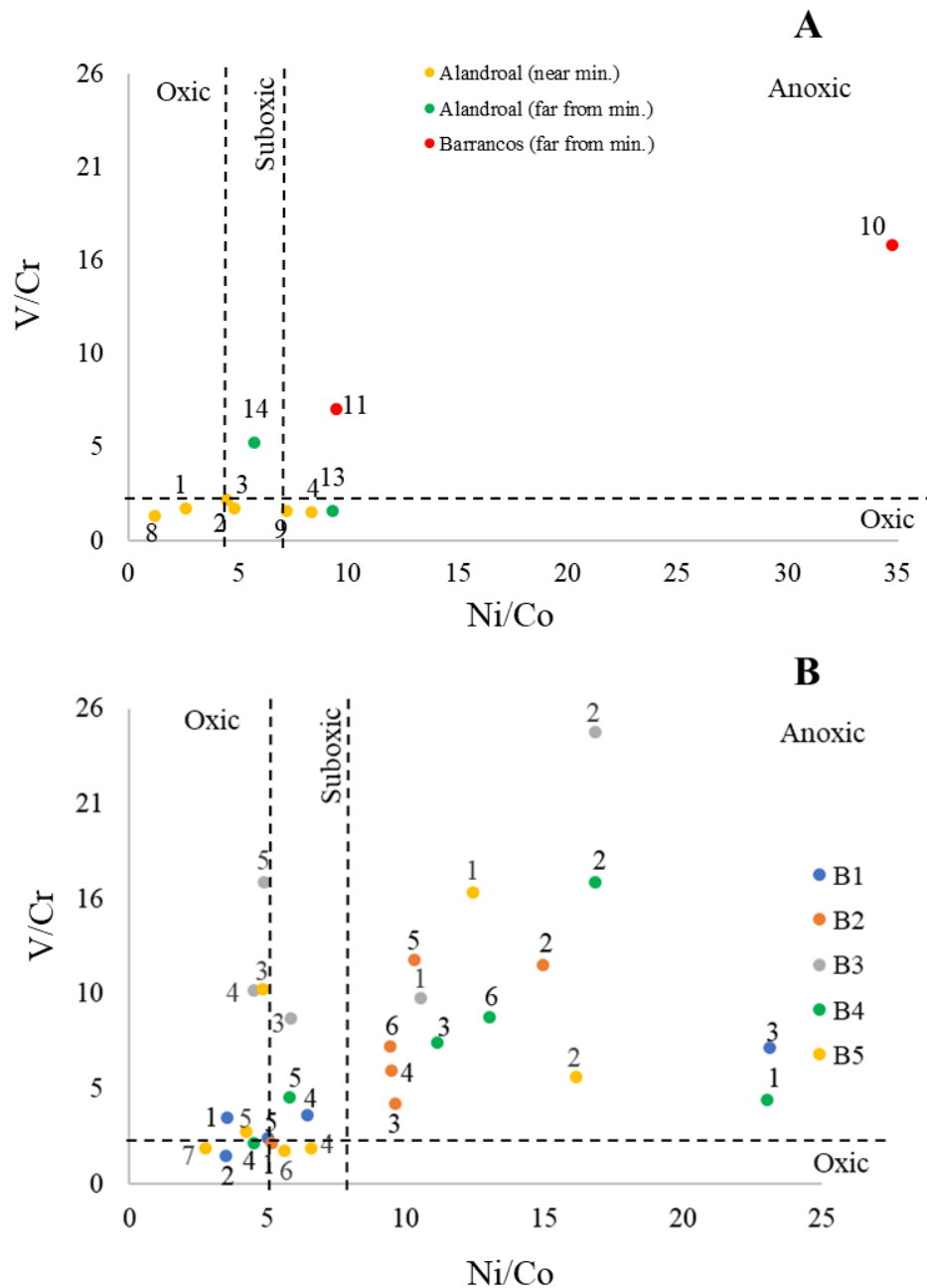


Figure 33 - Cross plot of trace element ratios used as paleoredox proxies (adapted from Rimmer, 2004). Ranges for V/Cr and Ni/Co are from Jones and Manning (1994). A) Samples from outcrops; B) Samples from Miguel Vacas drill cores.

Considering the Th/U ratio, Th is relatively immobile in the low-temperature surface environment, being concentrated during weathering in resistant minerals and is usually found in the detrital fraction associated with heavy minerals or clays (Jones and Manning, 1994). On the other hand, U may be fixed under reducing conditions (Jones and Manning, 1994). Consequently, values of $Th/U < 2$ represent anoxic conditions. According to this ratio, both samples from Barrancos (ZOM 10 and ZOM 11) and the majority of samples from Miguel Vacas drill cores seems to be deposited in anoxic conditions (Table 15), with exception of eight samples (B1_1, B1_2, B1_5, B4_4, B5_4 to B5_7).

The ratios Ni/Co, V/Cr and Th/U (Table 15) reveal that, generally, samples from Alandroal (far from mineralization) and Barrancos seems to be deposited in an anoxic depositional environment, while samples from Alandroal (near mineralization) have ratios that indicate their formation under oxic to suboxic conditions. The samples from Miguel Vacas do not have a consistent behavior, although the paleo-redox conditions ratios indicate that most of samples have been deposited in suboxic to anoxic conditions. Similar paleo-redox conditions were also described to the Silurian succession from OMZ (Piçarra, 2000; Robardet and Gutierrez-Marco, 2004; Roseiro et al., 2020), and also in several places around the world (e.g., Semtner and Klitzsch, 1994; Melchin, et al., 2012).

3.4.4. Organic matter and mineralization processes: what connection?

Organic matter can have a significant influence on the behavior of mineralizing systems (Greenwood et al., 2013). Previous studies provided evidence of a strong association between occurring minerals and OM (Greenwood et al., 2013) and, therefore, it is important the analysis of the variations of the elements and the TOC in the studied samples.

Figure 34 presents the concentration of selected elements to compare the general pattern between the regional background (Alandroal and Barrancos far from mineralization) with the samples near the mineralization in Alandroal region (including Miguel Vacas). In general, although similar concentrations are denoted, data show some particularities:

- the Ag and Cr median values of outcrop samples from Alandroal and Barrancos, far from mineralization, are generally higher when compared to the remaining samples, although maximum values were obtained in Miguel Vacas drill cores;
- median Cu concentrations are generally similar in all sample domains, but maximum values in Alandroal near mineralization and Miguel Vacas are around

- 10x superior as respect to the background, and minimum values are inferior to the minimum of background;
- the As content in Miguel Vacas is significantly higher when compared with other domains;
- the Co and Ni contents show similar behavior, with a significant increase of content in Alandroal near mineralization and Miguel Vacas; similar behavior is also identified in Fe content.

Pearson correlation coefficients allow to discuss some of the previous mentioned relations. The variation of Co and Ni concentrations indicates a positive correlation between these elements ($r = 0.73$, $p < 0.05$; Table 14). The high coefficients between both elements and P, S and Fe ($r > 0.5$, $p < 0.05$; Table 14) seems to indicate a possible association between phosphate phases and pyrite (which incorporate Co and Ni), possibly associated with organic-rich sedimentation of black shales. Although the coefficients between Ni, S and P, and TOC is significant ($r > 0.5$, $p < 0.05$; Table 14), similar behavior is not registered for Co ($r \approx 0.1$). The positive correlation between As and Ag contents in black shales ($r = 0.70$, $p < 0.05$; Table 14) seems to indicate their association to the same mineral phase. The increase of both elements should be related with the presence of dispersed sulfides (e.g., arsenic pyrite) in Miguel Vacas black shales related with ore deposit (Fig. 23C and 23D; Fig. 27). It should be emphasized that those phases are also identified in black shales from other areas, being associated with OM.

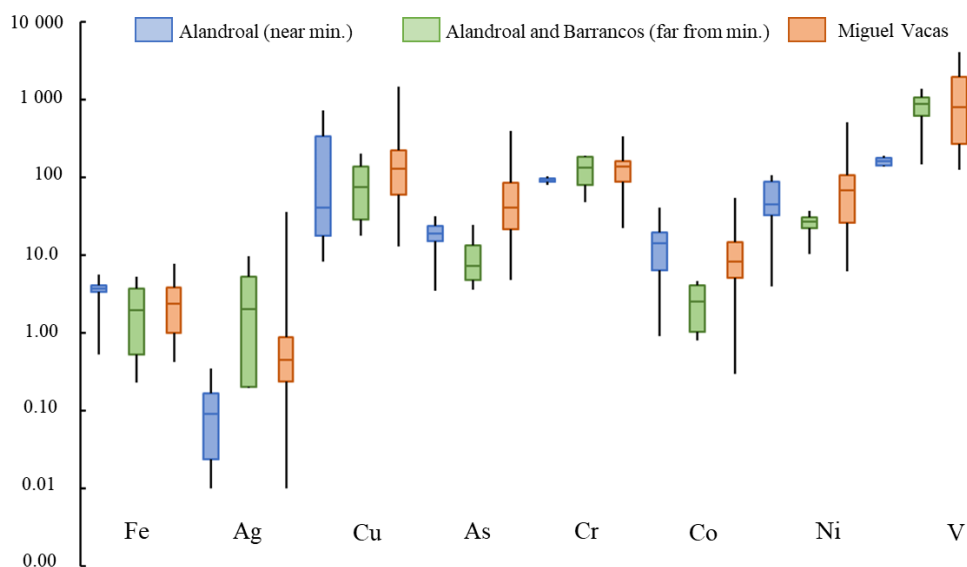


Figure 34 - Boxplots for Fe (%), Ag, As, Co, Cr, Cu, Ni, and V (ppm) content of outcrop and drill core samples.

In Figures 35 and 36 are presented the elemental variation profiles along the drill core samples from Miguel Vacas, with the representation of TOC, S, paleotemperatures, Fe, As, Cu, V and the paleoredox ratios Th/U and Ni/Co. The TOC content display vertical variations along the drill cores. Generally, the TOC peak is coincident with the peak of V, showing the association between both (also indicated by high values of CC; Table 13). The Cu profile also show great similarities with TOC, however the pattern is more variable. One meaningful feature of Cu pattern is the significative enrichment in Cu content around 50 m of drill core (around 35 m deep), being highly pronounced in B1, B2 and B3 (Fig. 35), reaching values between 500 - 1000 ppm. In those samples, Cu have CC ranging between 2 and 10 as respect to BBS. Similar pattern is also noted in Fe content. Except for the B4, where the Fe content generally increase with depth, the other drill cores show higher concentration of Fe between 30-50 m deep (Figs. 35 and 36), sometimes with concordant increase of As (B5; Fig. 36). The high concentration of Cu and Fe at this depth can be related with post-depositional processes, denoting the transition from oxidizing to reducing conditions (see also section 5.5.2.; Fig. 38).

The paleoredox ratios (Th/U and Ni/Co) show significative variations compatible with variations of TOC. Indeed, the increase of TOC values is consistent with the increase of Ni/Co ratio and the decrease of Th/U ratio (Figs. 35 and 36), denoting the preservation of OM during sedimentation of black shales in anoxic environment.

The paleotemperatures show an irregular pattern with the depth, which may indicate the presence of hydrothermal fluids (e.g., Barker, 1991; Glikson et al., 2000), promoting discrepant thermal evolution of OM in black shales. Thus, the pathway of hydrothermal fluids associated to mineralized Cu veins contributed to the discrepant maturation of OM, due to the percolation of the intermediate to high temperatures of fluids (Maia et al., 2019), and for the precipitation of metals, including those that are scattered in the host rocks.

Considering these results (Figs. 35 and 36) together with the mineralogical information (Table 16), and the available published data with the description of the Cu deposit in the studied area (e.g., Fernandes, 2012; Mateus et al., 2013; Maia et al. 2020), it is possible to discuss the relation between all the parameters. Samples collected between 35 to 50 m depth have, in general, an enrichment in Fe, As, Cr, Cu, Ni, U, V and REE, together with the highest TOC and S values (Table 13; Figs. 35 and 36). This could indicate that these black shales were not primary enriched in metals but were enriched during post-depositional processes.

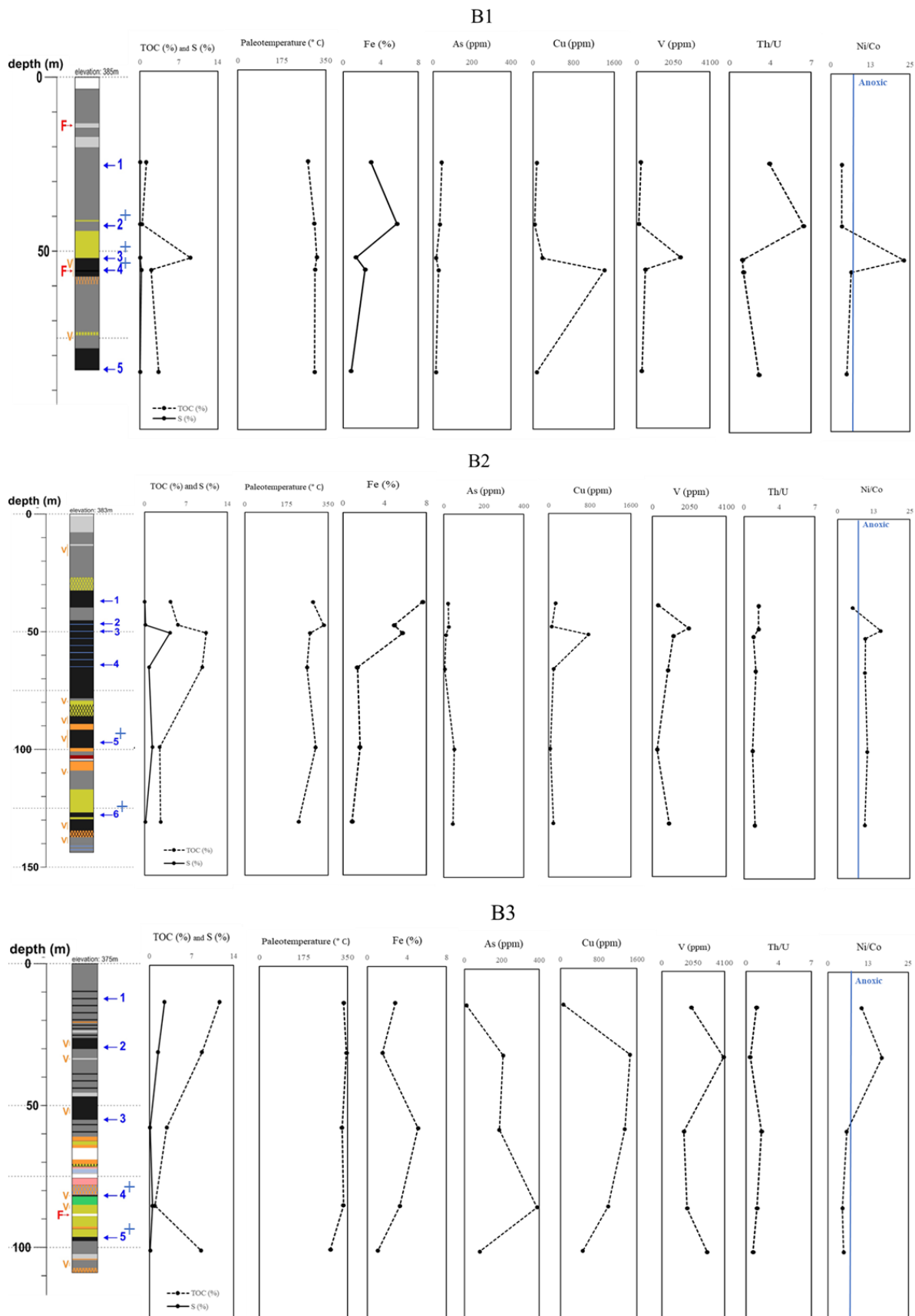


Figure 35 - Vertical variations of TOC, S, paleotemperatures, Fe, As, Cu and paleoredox ratios Th/U and Ni/Co from B1, B2 and B3 drill cores.

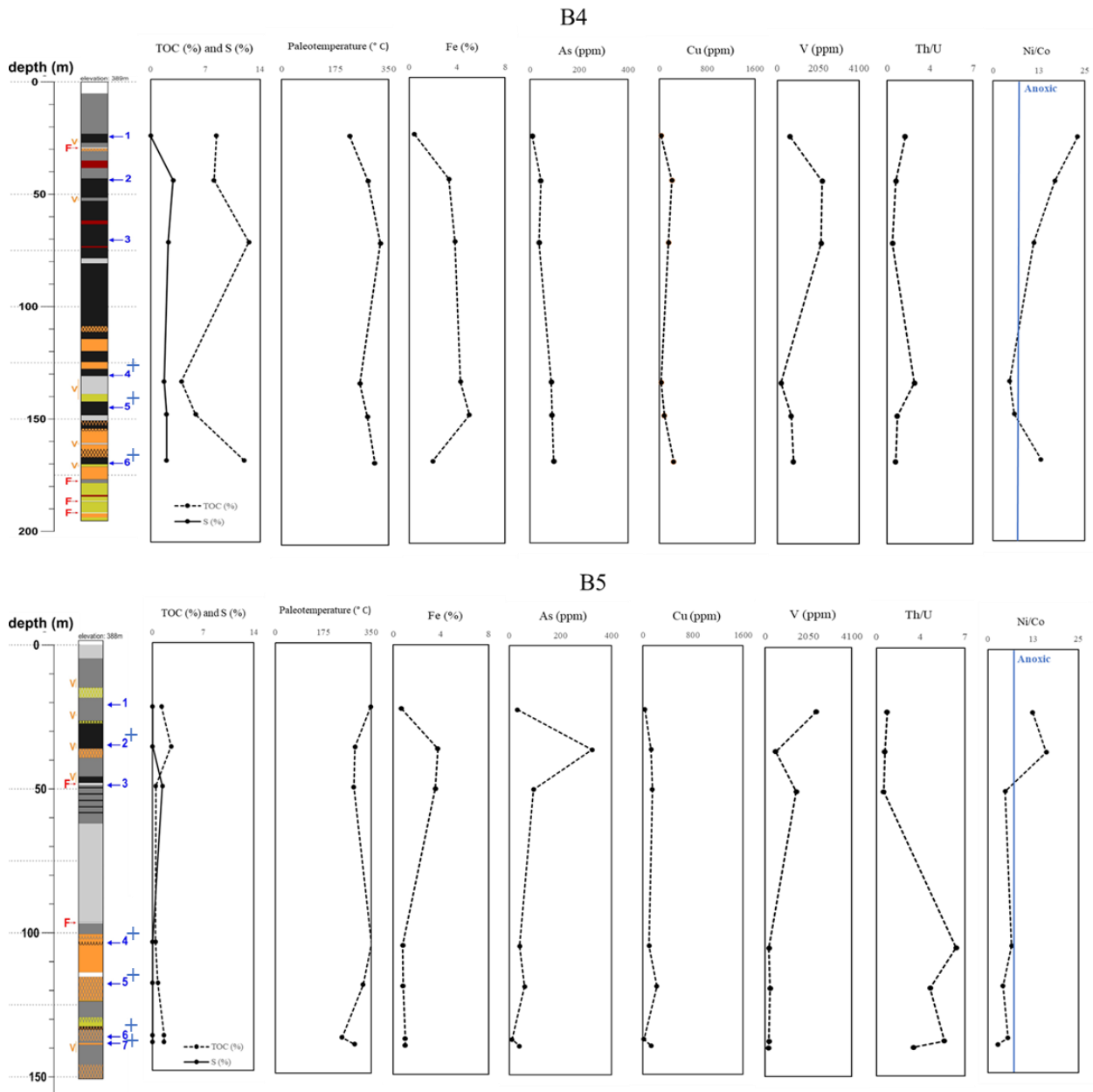


Figure 36 - Vertical variations of TOC, S, paleotemperatures, Fe As, Cu and paleoredox ratios Th/U and Ni/Co from drill cores B4 and B5.

Table 16 - Total organic carbon (TOC, %), proximity to mineralized veins, mineralogical information supplied by the company that provided the boreholes, and minerals identified by SEM-EDX in the studied black shales from drill cores in Miguel Vacas.

		Depth (m)	TOC	Proximity to mineralized veins	Mineralogical information	SEM-EDX
B1	1	25.4	1.14		Fe oxides and hydroxides	n.a
	2 ⁺	42.7	0.38	+	Fe oxides and hydroxides	n.a
	3 ⁺	52.1	9.1	+	Fe oxides and pyrite	Fe and Ti oxides. aluminosilicates. Ca phosphates.
	4 ⁺	55.5	2.04	+	Fe oxides and pyrite	n.a
	5	84.0	3.34		Fe oxides. quartz. carbonates and pyrite	n.a
B2	1	37.0	4.39		Fe oxides and quartz	n.a
	2	46.7	5.63		Fe oxides and pyrite	n.a
	3	49.9	10.4		n.a	Ca phosphates. pyrite. Cu sulfides
	4	64.1	9.73		n.a	n.a
	5 ⁺	97.1	2.56	+	Pyrite and chalcopyrite	n.a
	6 ⁺	128	2.71	+	Fe oxides. pyrite. and chalcopyrite	Ti oxides. aluminosilicates. Ca phosphates. pyrite
B3	1	12.4	11.7		Fe oxides and pyrite	n.a
	2	29.5	8.74		Pyrite and chalcopyrite	Quartz. pyrite. chalcopyrite. arsenopyrite
	3	55.0	2.87		Fe oxides. malachite. and pyrite	Ti oxides
	4 ⁺	81.5	0.9	+	Malachite and pyrite	n.a
	5 ⁺	96.6	8.58	+	Pyrite and chalcopyrite	n.a
B4	1	24.4	8.41		Fe oxides	n.a
	2	43.7	8.11		Pyrite	n.a
	3	70.4	12.6		Pyrite. chalcopyrite	Pyrite. chalcopyrite. arsenopyrite
	4 ⁺	131	3.96	+	Pyrite	n.a
	5 ⁺	145	5.76	+	Pyrite. chalcopyrite	n.a
	6 ⁺	170	11.9	+	Pyrite. chalcopyrite. ankerite	Pyrite. chalcopyrite. arsenopyrite
B5	1	22.3	1.27		n.a	n.a
	2 ⁺	36.3	2.59	+	Fe oxides	Fe oxides. Ca phosphates. aluminosilicates
	3	50.2	0.47		Fe oxides. pyrite	n.a
	4 ⁺	105	0.43	+	Pyrite. malachite. libethenite	n.a
	5 ⁺	119	0.76	+	Fe oxides. pyrite. chalcopyrite. ankerite. bornite	n.a
	6 ⁺	138	1.63	+	Pyrite. ankerite	n.a
	7 ⁺	140	1.61	+	Fe oxides. pyrite. ankerite	n.a

n.a - data not available.

3.4.5. Sousel-Barrancos metallogenic belt ores and the Miguel Vacas Cu deposit genesis

3.4.5.1. Discussing the regional scale ore deposits

The genesis of Cu deposits from Sousel-Barrancos metallogenic belt is not consensual. Two hypotheses were raised based on previous studies:

- (1) Several authors (e.g., Mateus et al., 2003, 2013; Tornos et al., 2004; Fernandes, 2012) suggest that the Cu content of Sousel-Barrancos ores was remobilized from Paleozoic metasediments, through hydrothermal chemically modified meteoric waters and residual metamorphic fluids, and later precipitated in vein-type structures. According to Mateus et al. (2003, 2013), the host Paleozoic rocks are pre-enriched in base metals. Other authors (e.g., Piçarra, 2000, Roseiro et al., 2020) also emphasizes that Silurian metasedimentary units were deposited in anoxic to euxinic depositional environment, which benefited Cu pre-concentration as sulfide phases, or in OM by chelation.
- (2) Recently, Maia et al. (2019, 2020) propose a revised model for Sousel-Barrancos metallogenic belt Cu-deposits, stating that the fluids found in the Mociços and other Cu-deposits in the region could be linked with a deep-seated magmatic body, that may be similar to other Late Carboniferous-Permian calc-alkaline igneous bodies of the OMZ (e.g., Santa Eulália Igneous Complex or the Alcáçovas - Baleizão porphyries). According to these authors, this deep-seated magmatic body is as possible source of hydrothermal fluids and possibly metals for Sousel-Barrancos metallogenic belt Cu-deposits. Although, the authors do not exclude the possibility of Paleozoic metasedimentary units also contributed as metal source in the Sousel-Barrancos ore deposits.

The data herein presented show an irregular maturation of OM (Table 9, Figs. 32 and 33) and concentration in elements patterns (Figs. 34, 35, and 36) at regional scale, both in the outcrop and drill core samples. As aforementioned, paleotemperatures obtained using the random mean reflectance values, indicate discrepant maturation of the OM particles along the Miguel Vacas drill cores, with temperature between 230°C and 345°C. This indicates that the maturation of the OM is not totally dependent of regional metamorphism and could be explained by the circulation of hydrothermal fluids of intermediate temperatures, associated with the formation of mineralized veins, in accordance with previous mentioned models (e.g., Maia et al., 2019; Laranjeira et al., 2019).

According to published data, the regional metamorphism in the Sousel-Barrancos Metallogenic Belt do not exceed the chlorite-biotite zones in the greenschist facies conditions (Perdigão et al., 1982; Oliveira, 1984; Pereira et al., 2012, Moreira et al., 2019), which is also in accordance with reflectance data obtained for the shale-derived rocks in the core of Estremoz Anticline (Laranjeira et al., 2023b) and with general values of reflectance and paleotemperatures presented in this paper. However, the spatial variance of reflectance values indicates discrepant spatial evolution. The reflectance values reveal that the maturation of OM in samples from Alandroal and Barrancos is generally higher (R_r between 3.0% to 4.5% and R_{max} between 5.0% to 6.5%) than samples from Miguel Vacas, collected along different drill cores, with the exception of samples B3_2 and B5_5. The spatial analysis within Alandroal area shows that values obtained in the Mociços region (R_r between 3.9% to 4.3% and R_{max} between 6.9% to 7.7%) are higher than: in Ferrarias (samples ZOM 8 and ZOM 9, R_r between 3.7% to 3.9% and R_{max} between 6.4% to 7.1%); the distal areas from mineralization occurrences located at West near Estremoz Anticline (R_r between 3.0% to 3.9% and R_{max} between 5.0% to 6.5%); and, values obtained in all samples from Miguel Vacas (R_r between 1.7% to 4.7% and R_{max} between 2.3% to 6.7%) (Fig. 37). As respect to Barrancos region, the obtained data reveal higher values of reflectance at NE (VR_{r-eq} 4.15% and VR_{max-eq} 5.31%), than in the SW sample (ZOM 11; VR_{r-eq} 3.13% and VR_{max-eq} 4.86). This can be the result of differential evolution of OM associated with spatial arrangement of regional and/or thermal metamorphism during the late tectono-metamorphic episodes of Variscan Cycle.

A possible presence of a deep-seated magmatic body controlling the late Paleozoic thermal evolution of Sousel-Barrancos Metallogenic Belt, as proposed by Maia et al (2020), could explain this spatial variation of maturation at regional scale (Fig. 37), but also: (1) the presence of a thermal metamorphism halo associated to an intense hydrothermal alteration in Zahinos and Oliva de la Frontera region; (2) the magnetic anomaly and the pseudo susceptibility pattern in Portugal and Spain, showing the presence of positive anomalies (e.g., Silva et al., 2000); (3) values of electrical resistivity model obtained by Almeida et al. (2001) which shows an intense and shallow anomaly underneath near the Mociços area; and (4) the nature of hydrothermal fluids associated to the Cu occurrences along this Metallogenic Belt (Maia et al., 2020). Therefore, OM reflectance data in Alandroal region seems to show a general increase of reflectance from NW to SE, toward the main anomaly of Zahinos-Oliva de la Frontera region (Fig. 37). Although with a smaller dataset, the spatial evolution of Barrancos region appears to show similar pattern with increase of paleotemperatures toward NE.

Local factors can also influence the thermal maturation of OM. Indeed, the samples from Ferrarias are located close to the Messejana fault (Fig. 37), where Mesozoic age doleritic rocks are described (Schermerhorn et al., 1978), explaining the higher values of maturation in this region. In Barrancos region (extending up until Mociços area), a igneous complex characterized by an association of lithologies comprising felsic and mafic volcanics, carbonates, and synsedimentary breccias are also described (Perdigão et al., 1982; Piçarra, 2000). The age of Barrancos Igneous Complex is unknown, but it is attributed to Upper Paleozoic.

However, there is also a considerable discrepancy between the values of reflectance (both R_r and R_{max}) in the outcrop samples from Alandroal area (near to mineralization) and in several samples from Miguel Vacas drill cores (Fig. 31), which cannot be explained by the previous described spatial variation of regional metamorphism effect. Indeed, fluid inclusion studies both in Mociços (Maia et al., 2019; 2020) and Miguel Vacas (Maia et al., 2019) deposits allow to constrain the minimum trapping temperatures of hydrothermal fluids associated with both deposits, showing a range of temperatures between 240°C and 420°C to Mociços, and between 180°C and 350°C to Miguel Vacas Cu vein deposit. These temperatures are consistent with maximum values of paleotemperatures estimated based on the reflectance of OM in the studied samples.

Therefore, the thermal maturation of the black shales from Sousel-Barrancos Metallogenic Belt seems be related with hydrothermal metamorphism, possibly associated with the deep-seated magmatic body as proposed by Maia et al. (2020). This magmatic body should be responsible for the P-T conditions during late tectono-metamorphic stages of the Variscan Cycle in this metallogenic belt and for supplying the hypersaline hydrothermal fluids responsible by the differential thermal maturation of OM associated with fluid circulation along host rocks, and probably associated with brittle-ductile Cu vein emplacement.

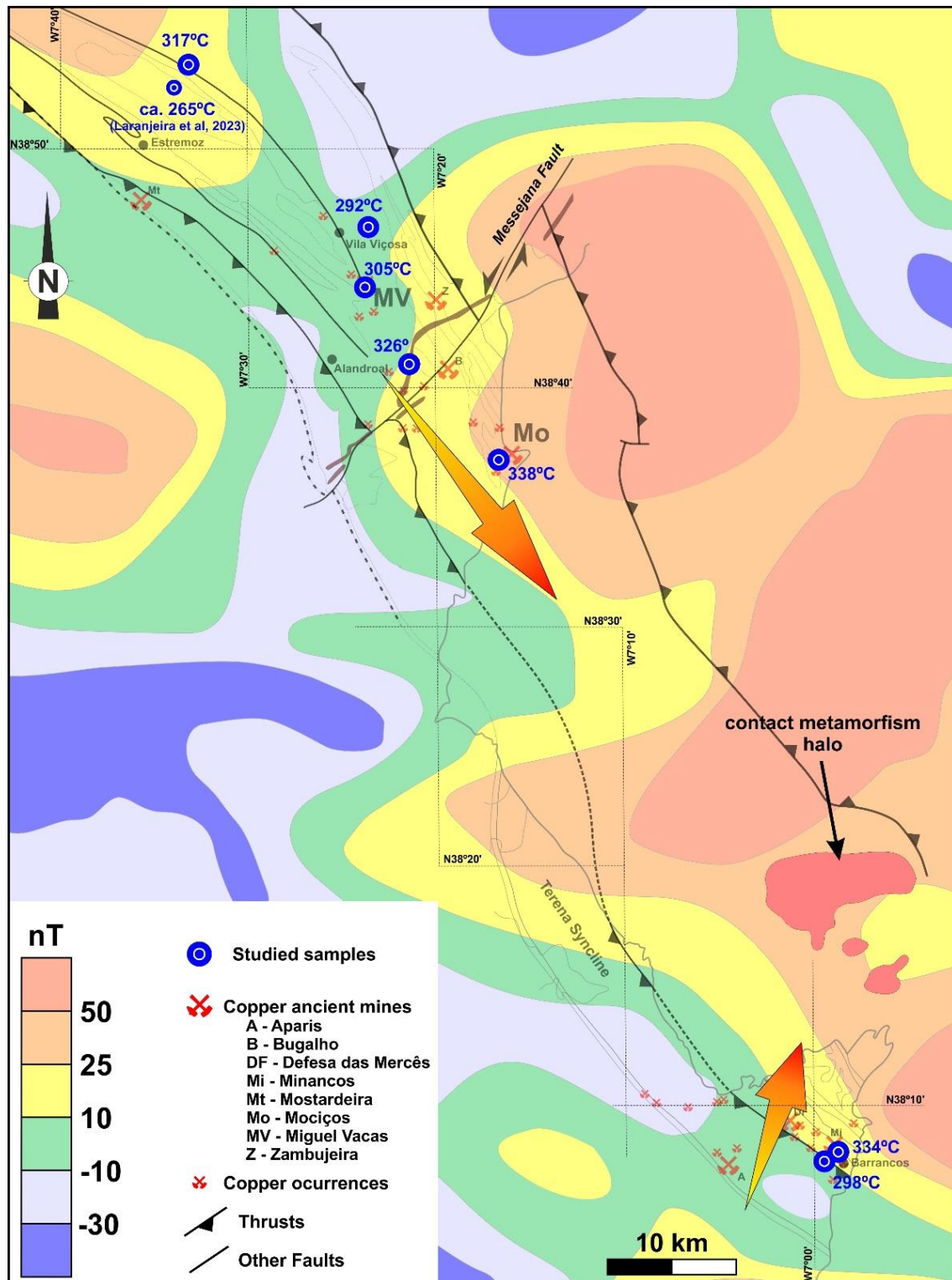


Figure 37 - Spatial disposition of black shale samples and the calculated paleotemperatures, overlaid to the magnetic anomaly pattern of Portugal and Spain (adapted from Silva et al., 2000).

3.4.5.2. Supergenic and primary enrichments domains in Miguel Vacas

The Miguel Vacas ancient mine is a Cu-rich vein crosscutting Silurian black shales (Mateus et al., 2003; 2013), where distinct vertical domains are identified (e.g., Fernandes, 2012; Mateus et al., 2003; 2013), from the surface zone to the deeper one (Fig. 38):

- Surface zone, characterized by Fe and Mn oxides and hydroxides accompanied by quartz evidencing strong oxidation; the abundant Fe oxides and hydroxides are the result of the leaching of the primary sulfides (chalcopyrite, pyrite and arsenopyrite) by the acidic and oxidizing conditions assisted by the meteoric water, which destabilize and deplete this zone of Cu phases.
- Supergene enrichment zone, that results from the reprecipitation of the leached Cu from the surface zone; the leached Cu occurs in two different forms (Guilbert and Park, 1986; Chávez, 2000; Robb, 2005; Sillitoe, 2005; Pohl, 2011): (1) in the more oxidizing domain, the ores are composed by secondary Cu minerals (oxides, carbonates, phosphates, sulfates) and Fe oxides, and (2) in the more reducing conditions, secondary Cu sulfides such as chalcocite, covellite and bornite occur, being accompanied by primary sulfides such as chalcopyrite, pyrite and arsenopyrite.
- Primary deposit domain, which mainly contains chalcopyrite, pyrite and arsenopyrite with no traces of alteration or secondary mineralization, such as secondary Fe and Cu phases.

Therefore, it is assumed that the primary mineralization results from the circulation of hydrothermal fluids, independently of their nature, not excluding the hypothesis that those fluids might remobilize metals from the surrounding rocks (Mateus et al., 2003; 2013; Fernandes, 2012; Maia et al., 2020). Presented data shows that there are some primary sulfides phases associated with OM, for example pyrite, chalcopyrite and arsenopyrite that were identified in petrographic studies. Additionally, no significant enrichment in Cu and other metals in the background samples were found. In the same way, our data does not exclude a hydrothermal fluid primary enriched in metals.

This Fe + Cu ± As ± Ag rich hydrothermal fluid, in favorable physical and chemical conditions, generates the primary sulfides phases, probably associated with the brittle controlled fracture zones (e.g., Mociços and Miguel Vacas) during the late Variscan deformation event (Maia et al., 2020). In this case, the black shales, more specifically

the OM and the associated S, can act as a redox changing environment promoting the precipitation of primary metallic sulfide phases (Pasava et al., 2008).

Afterwards, the meteoric-derived fluids remobilize metals from the vein, but also from Silurian host rock formations in the most superficial oxidizing zones. As such, Cu is remobilized from superficial zones and transported to deeper ones, but Fe will be concentrated in the Gossan zone as iron oxides and hydroxides (Fig. 38). In depth, the redox conditions change, and Cu finds the optimal conditions to reprecipitate as secondary Cu minerals. In the studied samples, the enriched Cu black shales were identified between 35 to 50 m deep (50 to 70 m in the drill cores), probably corresponding to the transition between surface oxidizing zone and the reducing zone (Fig. 38). Sometimes very close to the oxidation-reduction zone (equivalent to around 35 to 50 m deep), some Ag-rich levels are also locally found. This behavior was also described in previous papers for other enrichment type deposits (e.g., Velasco et al., 2013). The Ag content in analyzed black shales has high correlation coefficient with As (Table 14), allowing to consider its association with the presence of sulfides as arsenopyrite or arsenic pyrite. Consequently, a portion of Cu was removed from the mineralized veins, which were in an oxidizing environment, and was transported by meteoric-derived fluids and re-precipitated under reducing conditions, in the form of secondary Cu phases, as previously reported (Fernandes, 2012).

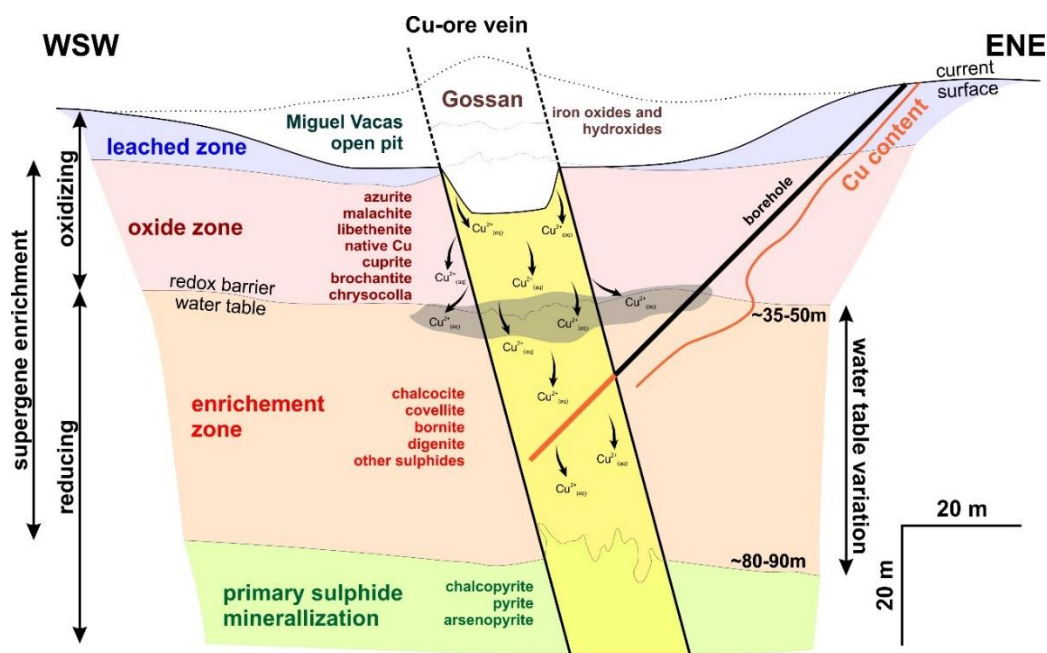


Figure 38 - Schematic cross section of Miguel Vacas ancient mine, emphasizing the distinct ore minerals in depth and the oxidizing and reducing domains (general model adapted from Pohl, 2011 and Fernandes, 2012).

3.5. Conclusions

Samples of Silurian black shales from OMZ, spatially associated with Cu mineralizations in Sousel-Barrancos metallogenic belt, were studied through petrography and geochemistry to understand their relationship with the processes that led to the formation of ore deposits, highlighting the role of OM.

Redox sensitive indicate that almost all black shale samples were deposited in suboxic to anoxic conditions. The Pearson correlation coefficients between TOC and S with metals as Fe, Cu, As and Ag suggests that those elements are not primary related with OM. A higher level of Cu enrichment was identified in some black shale samples collected in drill cores intercepting the Miguel Vacas Cu vein, being probably related with supergene enrichment processes. In Miguel Vacas, the Cu enrichment domain, together with the irregular maturation profiles, point the transition between superficial zone and the supergene enrichment zone around 35 to 50 m of depth. The samples corresponding to these levels also present, in general, an enrichment in some elements, together with higher concentrations of TOC and S that could be indicative that the black shales were not primary enriched in metals but were enriched during post-depositional processes.

The obtained results also indicated that the variation of thermal maturation in outcrop and drill core samples from Alandroal (including Miguel Vacas Cu deposit) and Barrancos regions can be interpreted as a result of the hydrothermal metamorphism. In the drill core samples from Miguel Vacas, it was identified an irregular profile of thermal maturation of OM associated to the pathway of hydrothermal fluids. The regional thermal evolution shows a spatial architecture compatible with the existence of a deep-seated magmatic body, as previously proposed by other authors, probably emplaced during late Variscan stages, which possibly generates magmatic-derived hydrothermal fluids responsible for the Sousel-Barrancos Cu deposits.

CHAPTER 4

CAMBRIAN BLACK SHALES FROM CENTRAL IBERIAN ZONE

Black shales spatially associated to a W-Skarn deposit from Douro Scheelite Belt (Portugal): insights from petrographic and geochemical studies.

Laranjeira, V., Ribeiro, J., Mendonça Filho, J. G., Flores, D. (submitted)

Abstract

In the Central Iberian Zone (CIZ, North of Portugal) occurs an important metallogenic W-Sn province, denominated Douro Scheelite Belt, where the W-Skarn Vila Seca-Santo Adrião deposit is included. The black shales from *Bateiras* Formation that occur spatially associated with the deposit were investigated aiming the determination of their petrographic and geochemical composition, considering the organic and inorganic fractions, as well as to recognize the relation with the mineralization. The petrographic study allowed the identification of scarce OM as vitrinite-like particles. The maturation of OM corresponds to anthracite to meta-anthracite, and paleotemperatures between 255°C and 324°C were estimated. The variable maturation of OM indicates the differentiated effect of metamorphic/metasomatic processes associated with skarns formation related with granitic body installation. Considering the geochemical composition and elements mode of occurrence, the enrichment in REE and Cs is the most notorious followed by As, Be, and Li, possibly associated with the contribution of granitic rocks installation and related fluids. From the Pearson correlation coefficients stands out the organic affinity of some elements and the association of S with sulfides. The association of elements with aluminosilicates, carbonates and phosphates was also identified. The ratio between redox sensitive elements revealed the prevalence of oxic conditions but a tendency to anoxic conditions was also predicted in some samples.

4.1. Geological framework

The CIZ is the largest geotectonic zone in the Iberian Massif and is located in the central part of the Iberian Terrain. It contacts tectonically the Galicia-Trás-os-Montes Zone (GTMZ) to the northwest, the West Asturian Leonese Zone to the northeast and the Ossa-Morena Zone to the south (by the Tomar-Badajoz-Córdoba shear zone) (e.g., Lotze, 1945; Julivert et al., 1972; Farias et al., 1987) (Fig. 39).

The CIZ and GTMZ are the geotectonic zones in which there are more deposits of W and Sn and the occurrence of granites is noticeable, being the correlation between mineralizations and granites recognized (e.g., Noronha et al., 2013). These zones are characterized by the syn-orogenic magmatism, in parallel with areas of intermediate to high metamorphic grade (Martinez et al., 1988; Ugidos, 1990). In this context, the granitic magmas played an important role in the thermal evolution in the CIZ and GTMZ (e.g., Noronha et al., 2013). The CIZ is characterized by the abundance of Variscan granites intruding the metasedimentary rocks of the Upper Proterozoic and Lower Paleozoic, comprising several lithologies, including some carbonate-rich levels (Dias et al. 1998).

The occurrences of Sn, W and Au in northern Portugal show a distribution according to alignments parallel to the Variscan orogenic structure and the granite massifs, and to late-Variscan fracturing systems (Noronha et al., 2013).

The metasedimentary sequences in CIZ are mainly represented by the Durico-Beirão Supergroup, which is composed by the Douro Group and Beiras Group. The Douro Group (Fig. 40) presents a lower Cambrian age, and is essentially constituted by intercalations of schists, greywackes, metapelites, calcossilicate rocks, limestones, and microconglomerates (Sousa et al., 1982; Sousa and Sequeira, 1989). The Douro Group is composed by *Bateiras* and *Ervedosa do Douro* Formations - autochthonous units, and by *Rio Pinhão*, *Pinhão*, *Desejosa* and *S. Domingos* Formations - allochthonous units (Silva and Ribeiro, 1985 in Sousa and Sequeira, 1989).

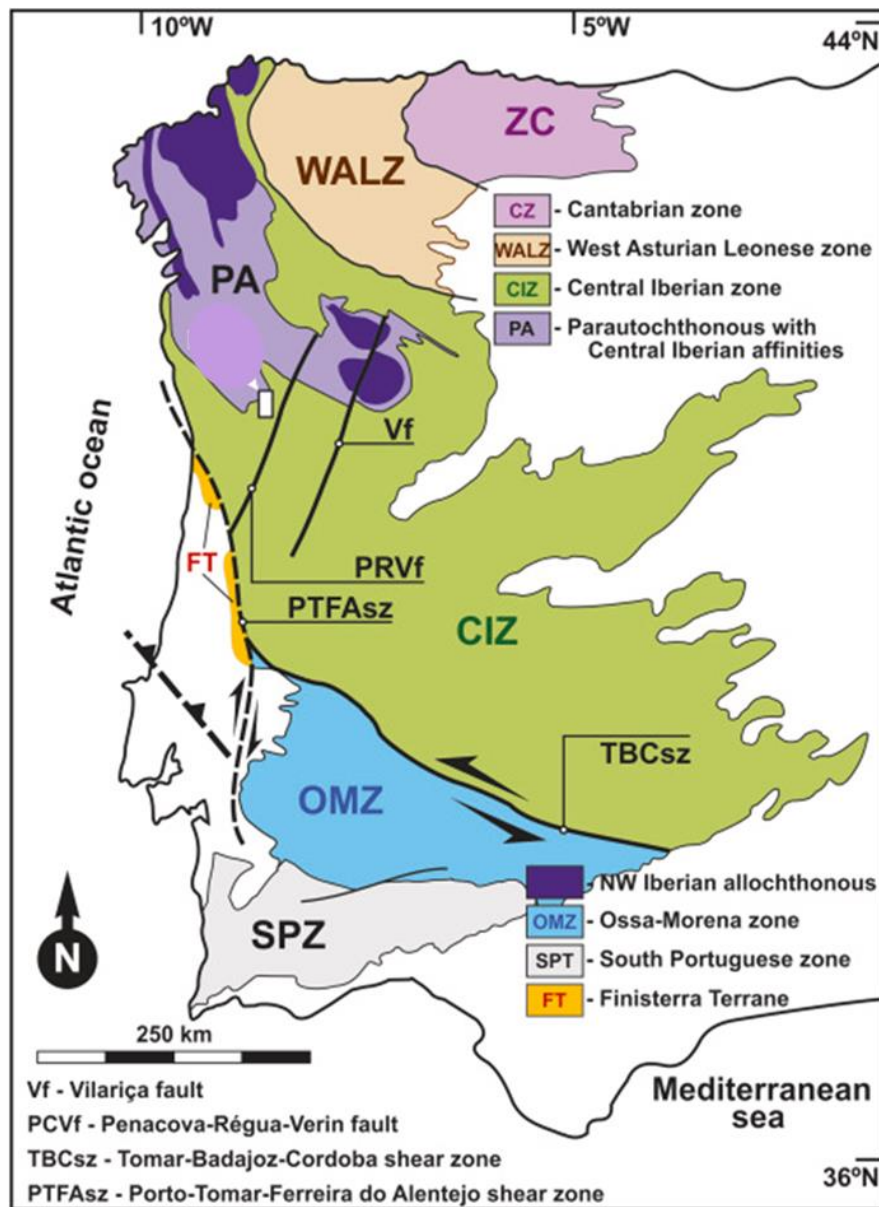


Figure 39 - Schematic geological map of the geotectonic zones of Portugal (adapted from Dias et al., 2022).

The *Bateiras* Formation is the oldest and the thickness of this unit is higher than 800 m (Sousa, 1982). It is characterized by the presence of graphitic black phyllites levels, metagreywacke and limestone that occur only in this unit. This unit is divided into two members: a lower member characterized by metagreywacke that contain a level of microconglomerates, followed by an alternation of metagreywacke with metrical thickness, with graphitic black phyllites (Sousa, 1982); and the upper member is characterized by the presence of limestones, gray phyllites and metagreywackes (Sousa, 1982).

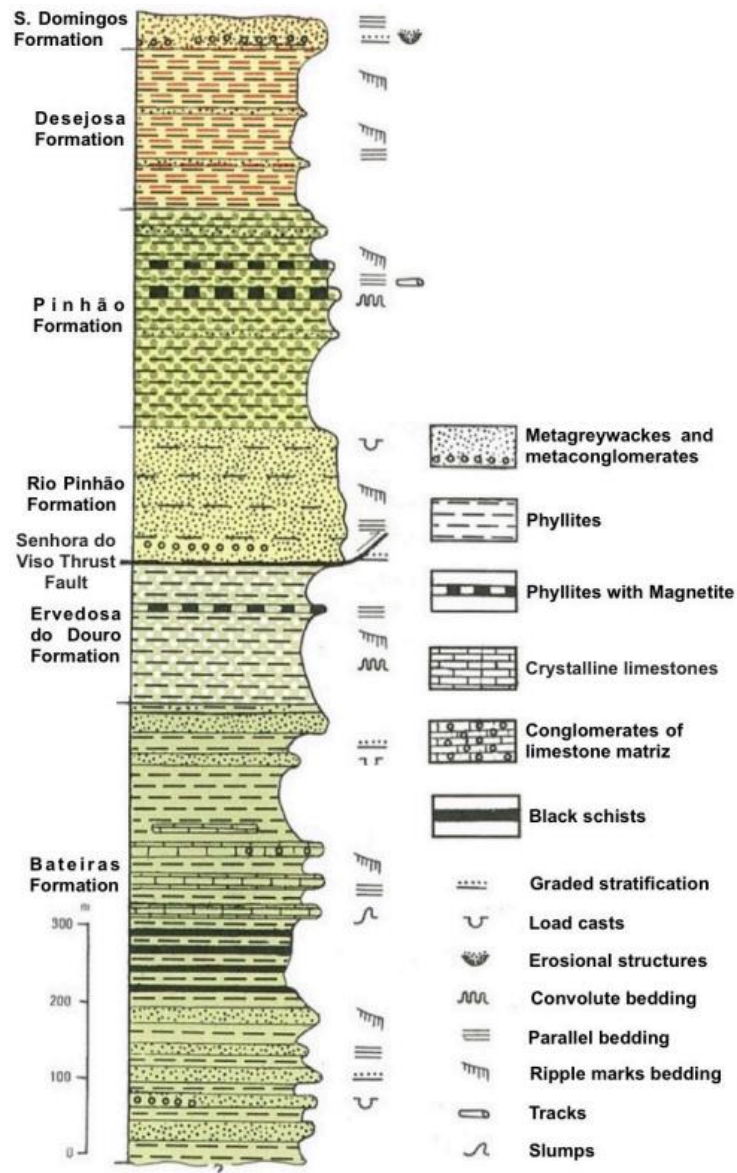


Figure 40 - General stratigraphic column of the Douro Group (from Gomes, 2016 after Sousa and Sequeira, 1989).

Skarns and calcosilicate rocks occur where the Douro Group is in contact with Variscan syn-orogenic granites. The W-skarns are mineralized with scheelite and are included in the Douro Scheelite Belt (DSB). Figure 41 shows the important mineralized domains in CIZ, including the DSB. The most important W-skarns deposits with scheelite in the DSB are São Pedro das Águias (Tabuaço) and Vila Seca-Santo Adrião (Armamar) (e.g., Ramos et al., 2017). Among the recognized deposits, the black shales from *Bateiras* Formation, spatially associated with the Vila Seca-Santo Adrião deposit, were investigated in this research paper.

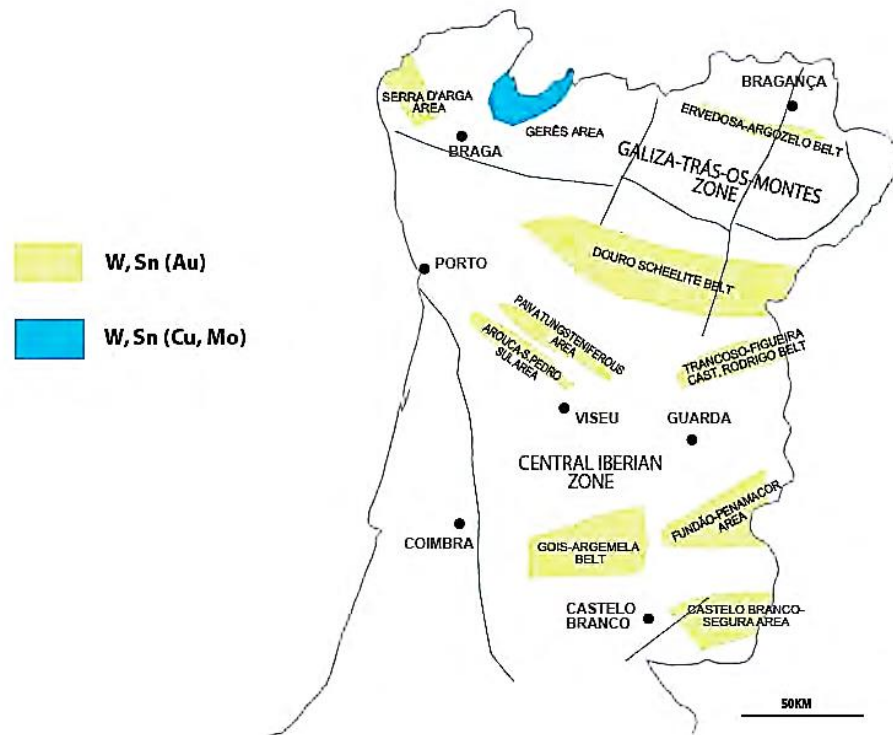


Figure 41 - Distribution of mains W and Sn mineralizations in Portugal, including the Douro Scheelite Belt (from Martins, 2012).

The lithologies occurring in association with Vila Seca-Santo Adrião deposit are typical of the CIZ flysch-type units represented by greywackes, shales, and schists of late Precambrian to Cambrian age (Fig. 42; Sousa and Sequeira, 1989; Golder Associates, 2020). Syn-metamorphic muscovite-biotite granites or post-metamorphic biotite rich granites intruded the flysch sequence (Sousa and Sequeira, 1989; Golder Associates, 2020). This deposit is formed by some levels of metric skarns (with 2 to 30 m of thickness), generally well mineralized with scheelite, containing arsenopyrite and pyrrhotite, defining a sloping anticlinal structure. These levels are included in the *Bateiras* Formation, being the mineralized section equivalent to the levels of impure carbonate and limestone metagraywacke that overlap the last level of black shales (Fig. 40) (Sousa and Sequeira, 1989). The skarn zones represent metasomatized Ca-rich sediments, often associated with W mineralization.

Figure 43 shows the location of Vila Seca-Santo Adrião deposit and the area conceded for exploration by the Portuguese Government (DGEG, 2023).

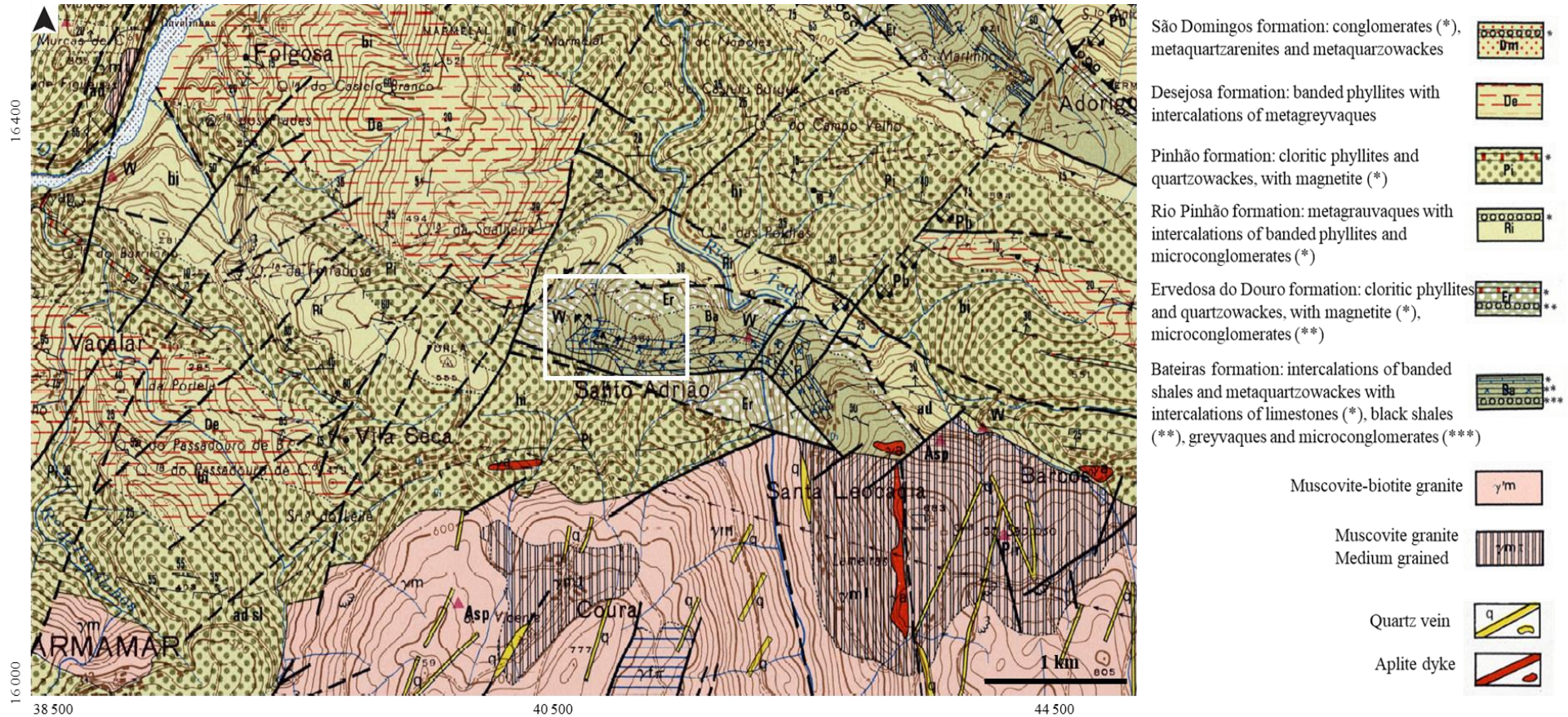


Figure 42 - Regional geology with approximate location of Vila Seca-Santo Adrião deposit (Sousa and Sequeira, 1989).

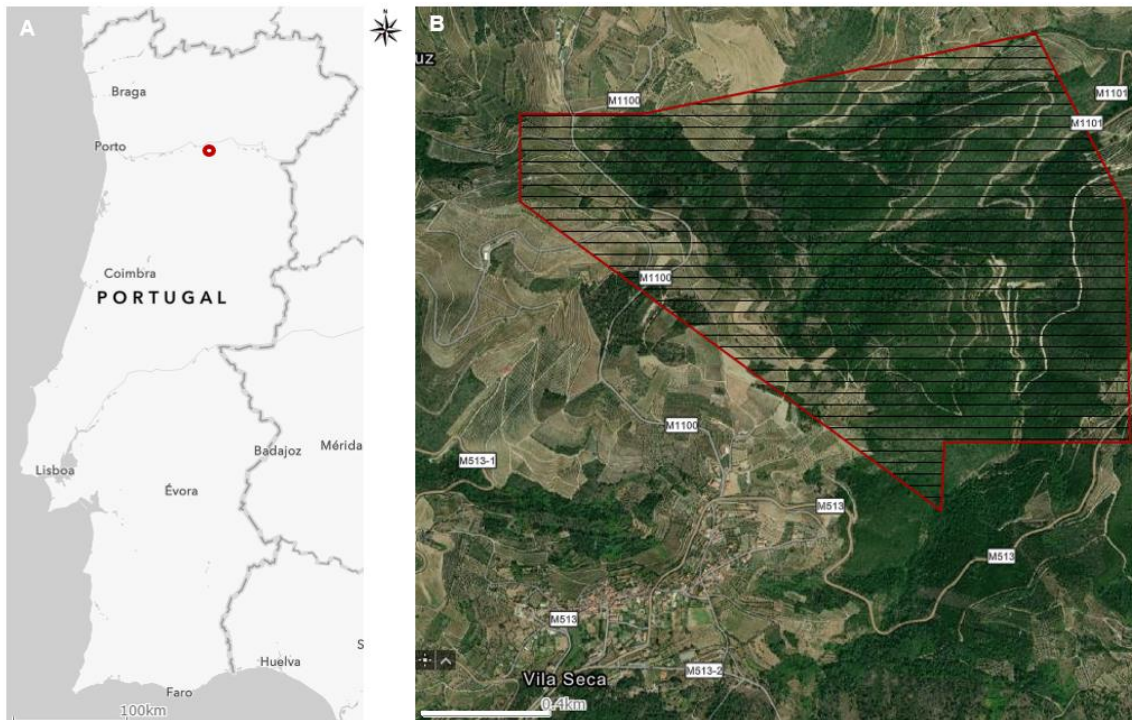


Figure 43 - A) Location of Vila Seca-Santo Adrião deposit (from GoogleEarth); B) Area conceded for exploration of Vila Seca-Santo Adrião by the Portuguese Government (DGEG, 2023).

4.2. Sampling

A total of 15 samples of black shales from *Bateiras* Formation occurring in association with Vila Seca-Santo Adrião deposit were collected: 2 outcropping (Fig. 44A) and 13 from drill cores. From the outcropping samples, A1 (Fig. 44B) was collected further from the contact with skarn, while sample A2 (Fig. 44C) was collected closer to the contact with skarn. The other samples were collected from drill cores obtained from five boreholes performed for exploration purposes by a private company in 2018. Some of these drill cores crosscut skarn levels with scheelite from the Vila Seca-Santo Adrião deposit.



Figure 44 - A) *Bateiras* Formation sampled outcrop; B) and C) Samples collected in the outcrop.

Figure 45 shows the location where exploration boreholes were performed, being the sampled drill cores identified with green dots (RGD 039, RGD 034, RGD 038, RGD 040 and RGD 035). Figure 45 also shows the location of outcropping skarn with scheelite and the interpreted skarns. The samples were selected from different depths along the drill cores, as described in Table 17. The description of sampled material given in Table 17 was based in the logging information provided by the private company that allowed the samples collection.

During sampling of outcropping black shales, the topmost layer has been removed to avoid weathered material. Samples from drill cores were selected considering the proximity to skarn levels reported in the logging information. The samples closest to skarns are located up to a maximum of 3.0 m from the reported levels and are marked with the symbol * (Table 17).

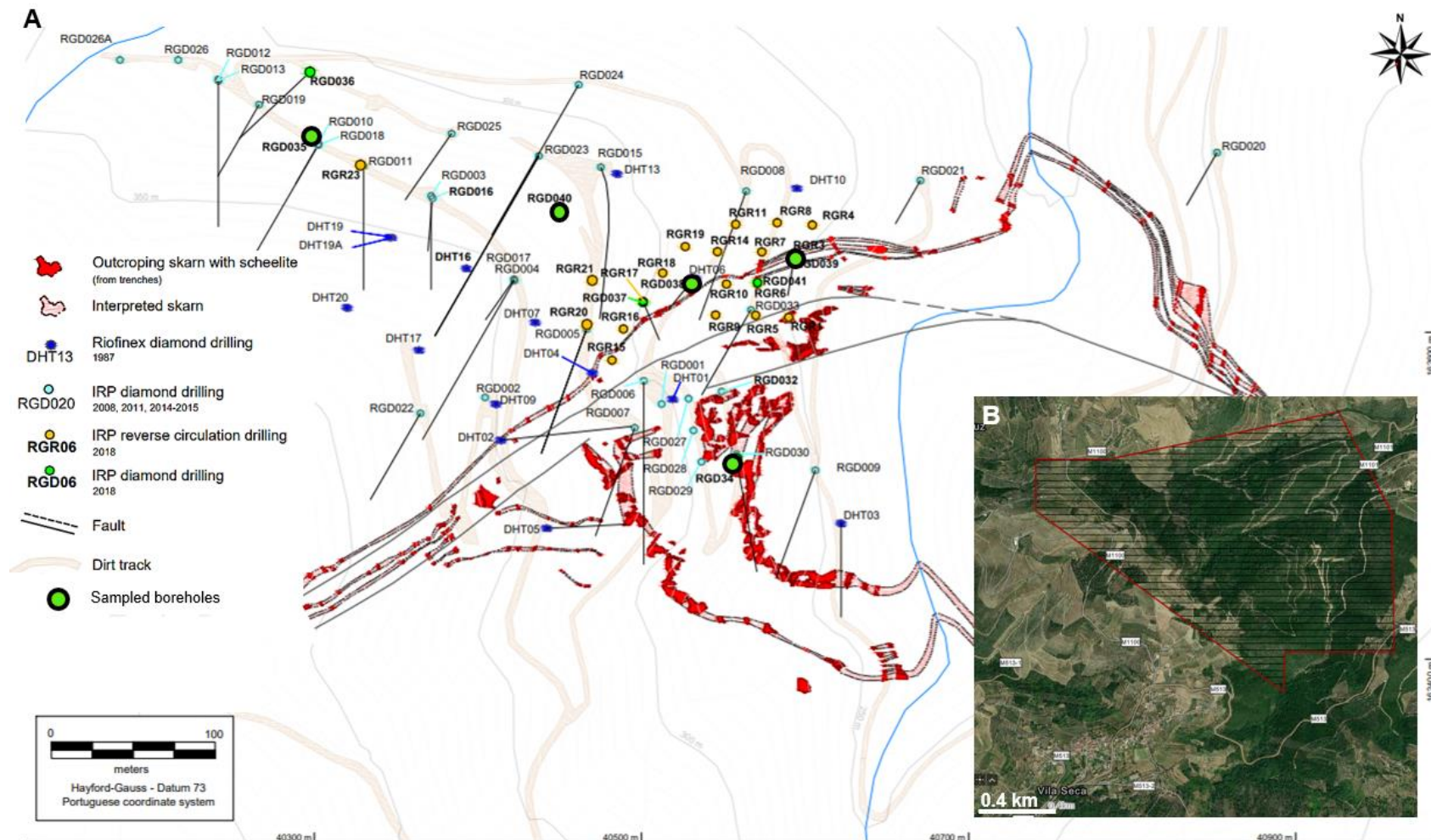


Figure 45 - A) Location and identification of the boreholes performed for exploration of Vila Seca-Santo Adrião deposit (adapted from information provided by the company); B) Area conceded for exploration of Vila Seca-Santo Adrião (DGEG, 2023), in which the boreholes were executed.

Table 17 - Systematization of sampling from drill cores.

Boreholes	Samples	Depth (m)	Description
RGD 039 (50.5 m depth)	A4	34.0	Intercalations of pyrite/pyrrhotite black shales and dark gray sericitic shales
	A3	41.0	Black shales
RGD 034 (140 m depth)	A6	51.2	Centimeter alternations of sericitic schists and black, pyrrhotitic shales
	A5*	90.0	Intercalations of black, pyrrhotite and pyrite shale, with calcosilicate rocks and skarns (above is skarn garnet - vesuvianite: 2.37 m thick)
	A7	122.5	Spotted sericitic, gray shale with thin layers of black, pyritic shales
RGD 038 (65.0 m depth)	A9*	28.2	Intercalations of black, pyrrhotite and spotted sericitic, gray shale (above occurs diopside - epidote skarns: 1.88 m thick)
	A8	41.5	Black shales, pyrite, with passages of spotted sericitic, gray shale
RGD 040 (160 m depth)	A10*	89.8	Centimeter alternations of sericitic, gray and black pyritic shales (above is skarn garnet - vesuvianite: 0.68 m thick)
	A11	110.8	Black, graphite, pyrite and pyrrhotite shales
	A12	155.8	Alternations of sericitic, gray and black, pyrite, graphite shales
RGD 035 (200 m depth)	A13	96.0	Black, pyritic shales, with centimeter passages of sericitic shale
	A14*	159.0	Intercalations of black, pyritic and pyrrhotitic shales, with levels of hornfel and skarn (above: 2.82 m thick and below 3.08 m thick diopside - epidote skarns)
	A15	186.0	Sericitic, gray schists with passages of metagraywackes and levels of black, pyritic shales

* Black shale samples collected nearest skarn levels.

Figure 46 shows the macroscopic aspect of some of the selected black shales.



Figure 46 - Macroscopic view of samples A3 e A8.

4.3. Results and discussion

4.3.1. Petrographic characterization of organic and inorganic matter

Through the petrographic observations of the studied black shales, it was identified vitrinite-like particles in all samples, although in some of them the organic particles are scarce and very small. In general, the vitrinite-like particles are thin and elongated, occurring interbedded with mineral matter (Fig. 47). The mode of occurrence of OM in the different drill cores and the outcrop samples are similar (Fig. 48). Some particles exhibit graphitic features, being larger in size, and occurring as single flakes (Fig. 48).

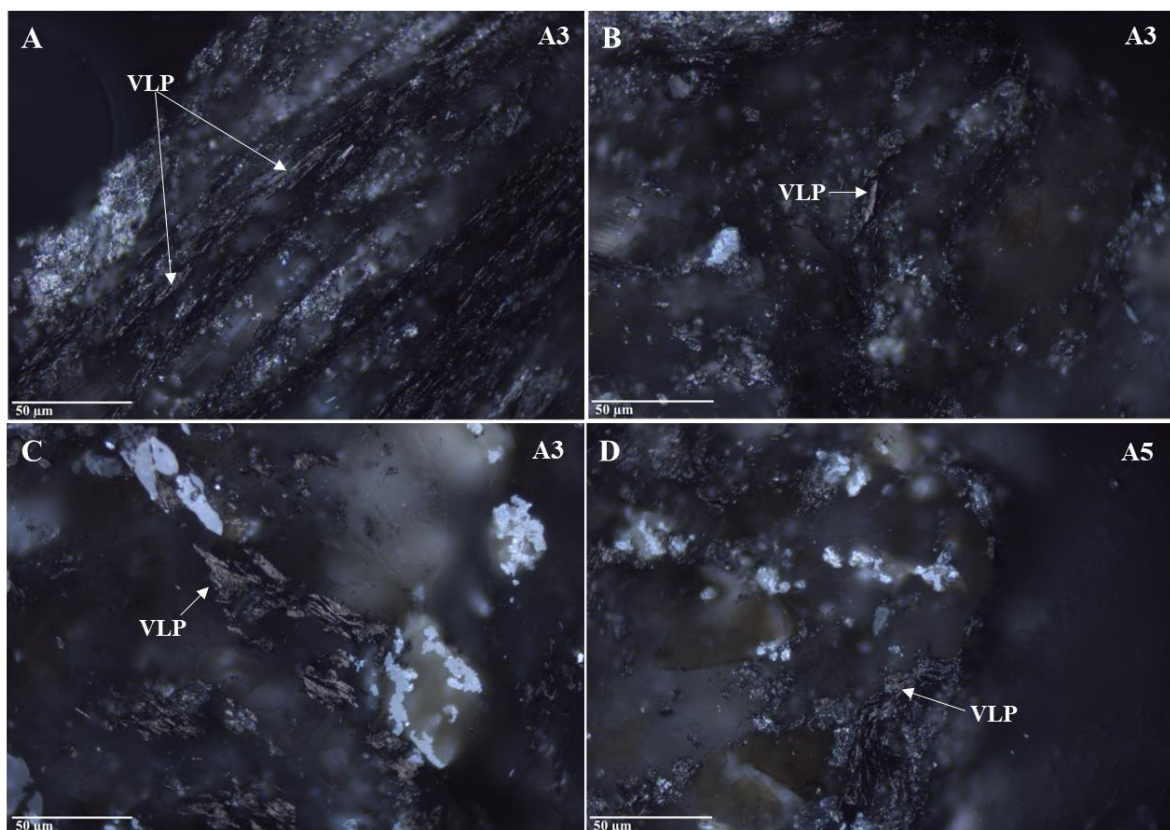


Figure 47 - A) to D) Photomicrographs showing vitrinite-like particles (VLP) thin and small, occurring along with mineral matter. Photomicrographs taken in reflected white light and 50x immersion oil objective.

The petrographic analysis allowed the observation of detrital derived minerals, mainly quartz and phyllosilicates, occurring in association with OM, and also the presence of iron oxides and sulfides. However, there are differences among the samples: in samples A1, A2, A3, A4 and A15 the presence of iron oxides is more evident when compared to the other samples (Fig. 49), while in samples A5, A8 and A9 the presence of sulfides

stands out (Fig. 50). In the other samples (A6, A7, A10, A11, A12, A13 and A14) is more evident a siliceous component.

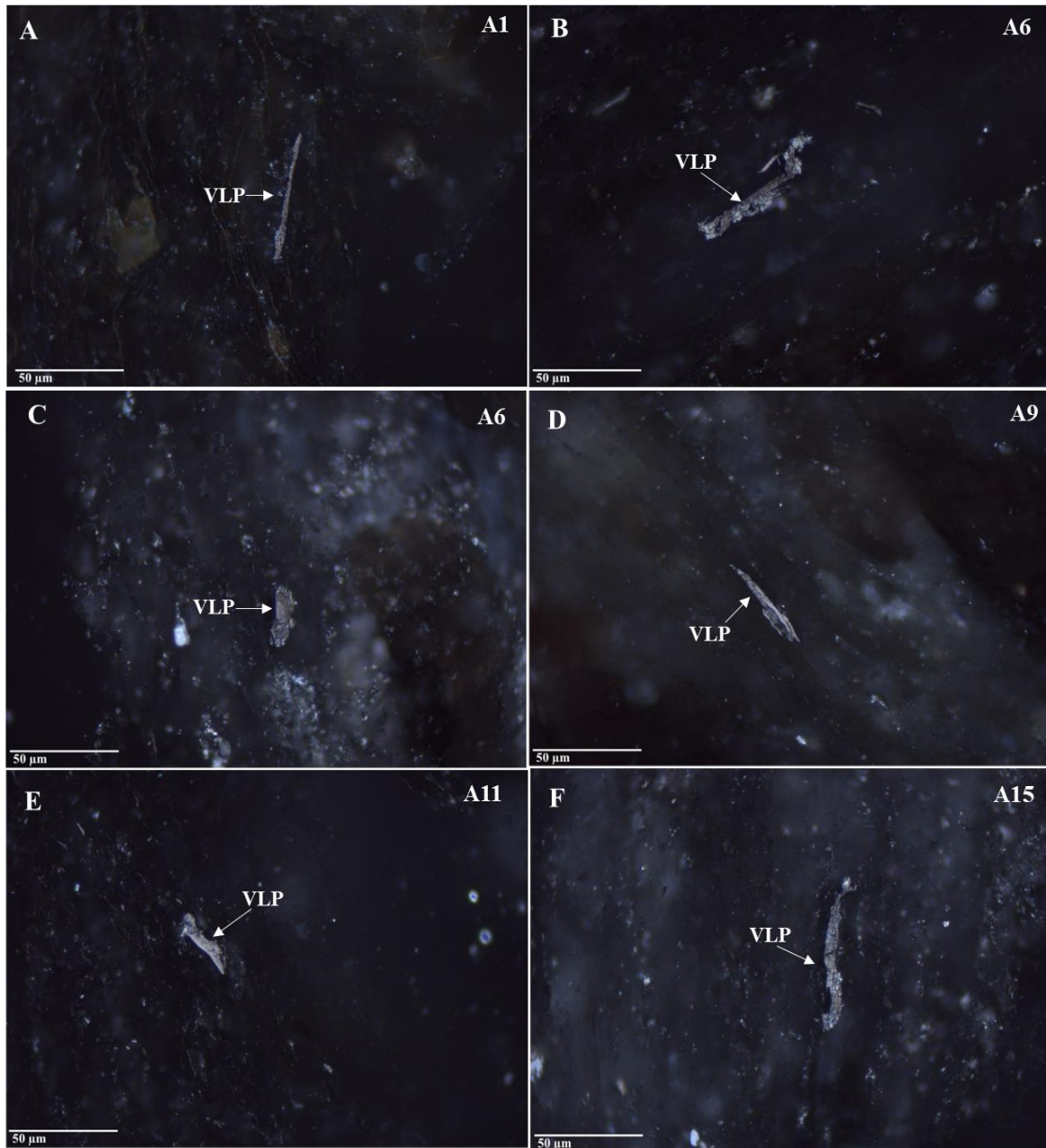


Figure 48 - A) to F) Photomicrographs of vitrinite-like particles (VLP) exhibiting graphitic structures and occurring as single flakes. Photomicrographs taken in reflected white light and 50x immersion oil objective.

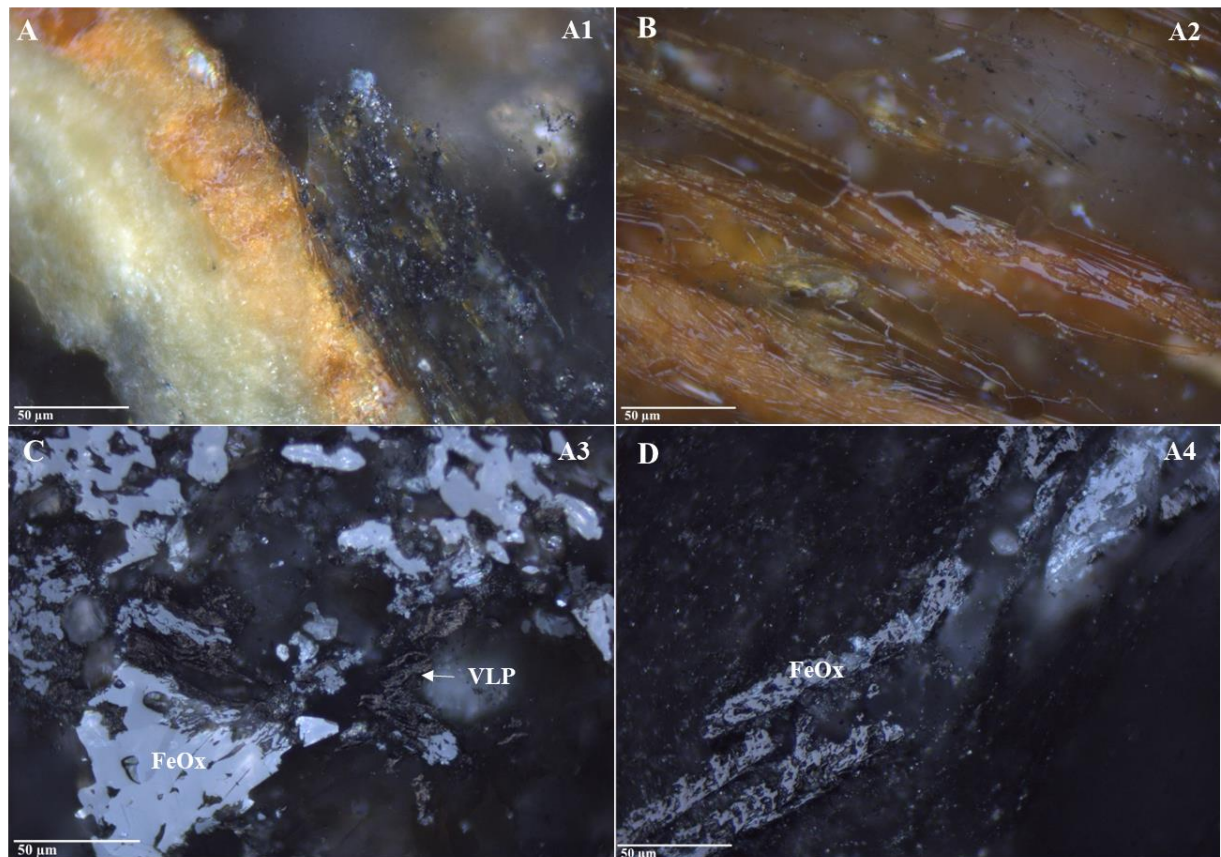


Figure 49 - A) to D) Photomicrographs of iron oxides (FeOx) in samples A1 to A4. Photomicrographs taken in reflected white light and 50x immersion oil objective.

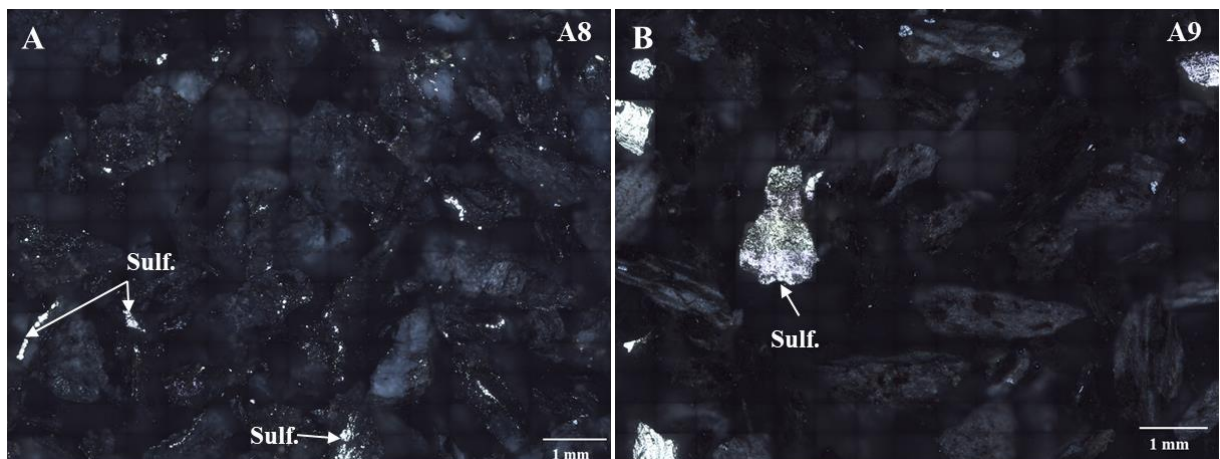


Figure 50 - A) and B) Mosaics prepared from the assembly of photomicrographs taken from the polished blocks, exhibiting the petrographic general view of occurrence of sulfides (Sulf.) in samples A8 and A9. Photomicrographs taken in reflected white light and 20x immersion oil objective.

SEM-EDX analysis was performed in selected samples (from outcrop - A2; from drill cores - A3, A5, A6, A8, A9 and A10) to complement information about petrographic and mineralogical composition, and elements mode of occurrence. Aluminosilicates (Fig. 51, spectrum Z1), Ti oxides (Fig. 51, spectrum Z2), quartz and Fe sulfides, possibly pyrite, (Fig. 52A, spectrum Z1; Fig. 52B; Fig. 53, spectrum Z2; Fig. 54, spectrum Z2), were identified in all the observed samples.

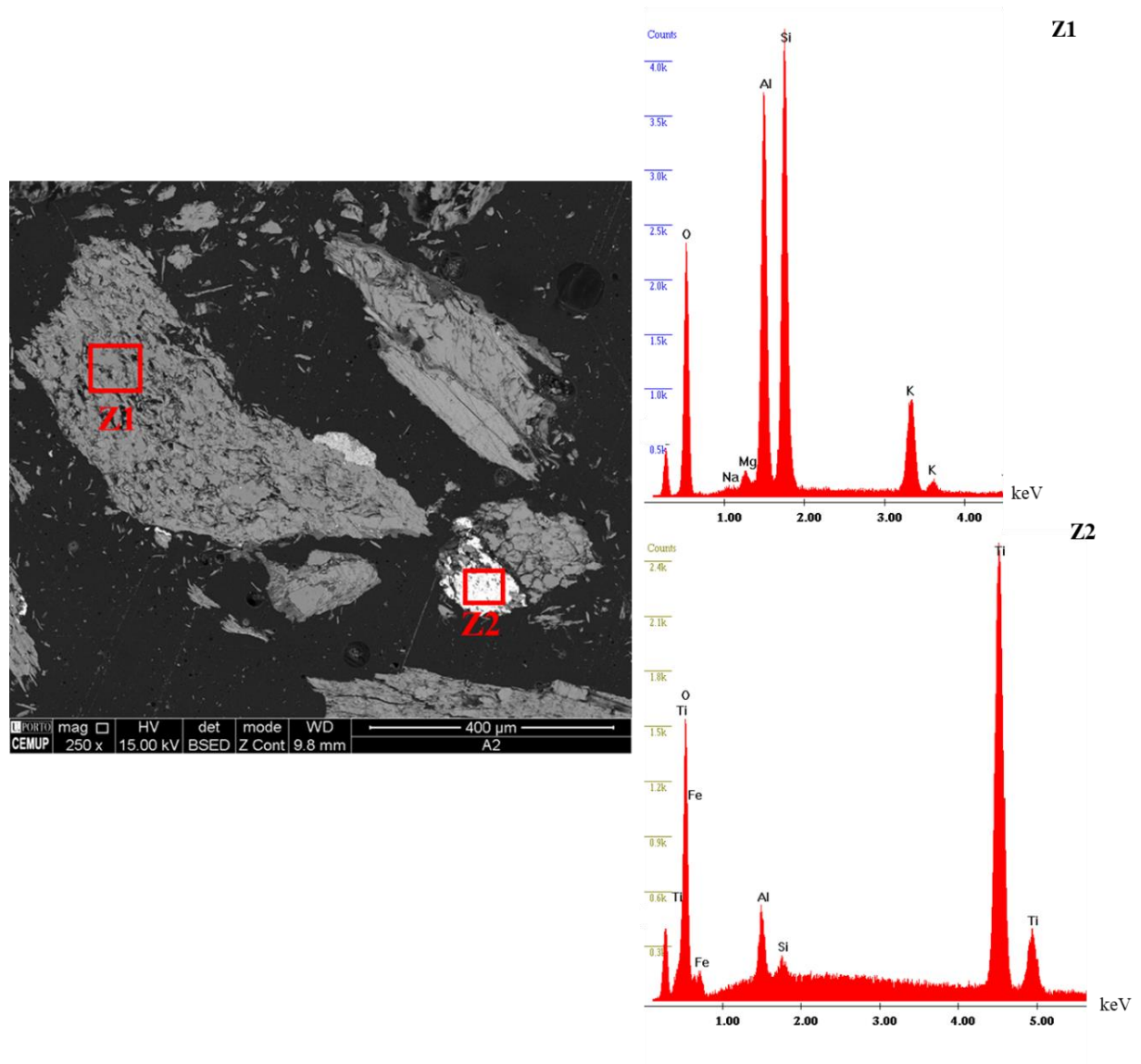


Figure 51 - SEM image and EDX spectra of aluminosilicates (Z1) and titanium oxides (Z2) in sample A2.

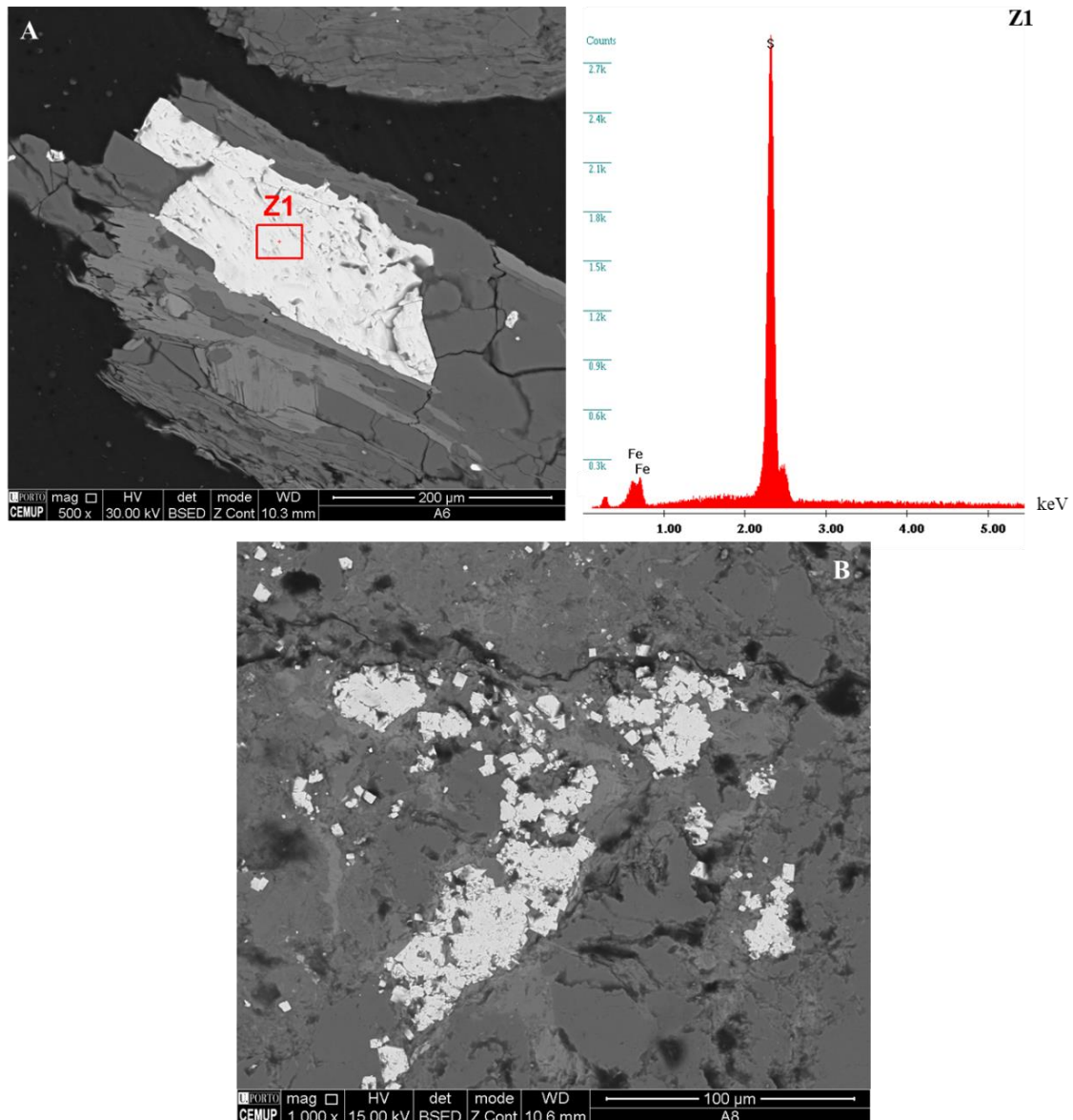


Figure 52 - SEM images: A) and EDX spectrum of Fe sulfide (Z1) in sample A6; B) Fe sulfide within aluminosilicates in sample A8.

The presence of arsenopyrite was recorded in samples A3 (Fig. 55, spectrum Z1), A5, and A9, whereas chalcopyrite was observed in samples A3, A6 and A8 (Fig. 55, spectrum Z2). In samples A3 and A5 it was also identified Pb sulfides, possibly galena (Fig. 53, spectrum Z1). The presence of Zn sulfides, likely sphalerite, was detected in all samples (Fig. 53, spectrum Z3), except in samples A2 and A5. The presence of REE phosphate was also observed in samples A6, A8 (Fig. 54, spectrum Z1) and A9. The mineral constituents found through SEM-EDX analysis are consistent with petrographic observations and with the described in the logging information.

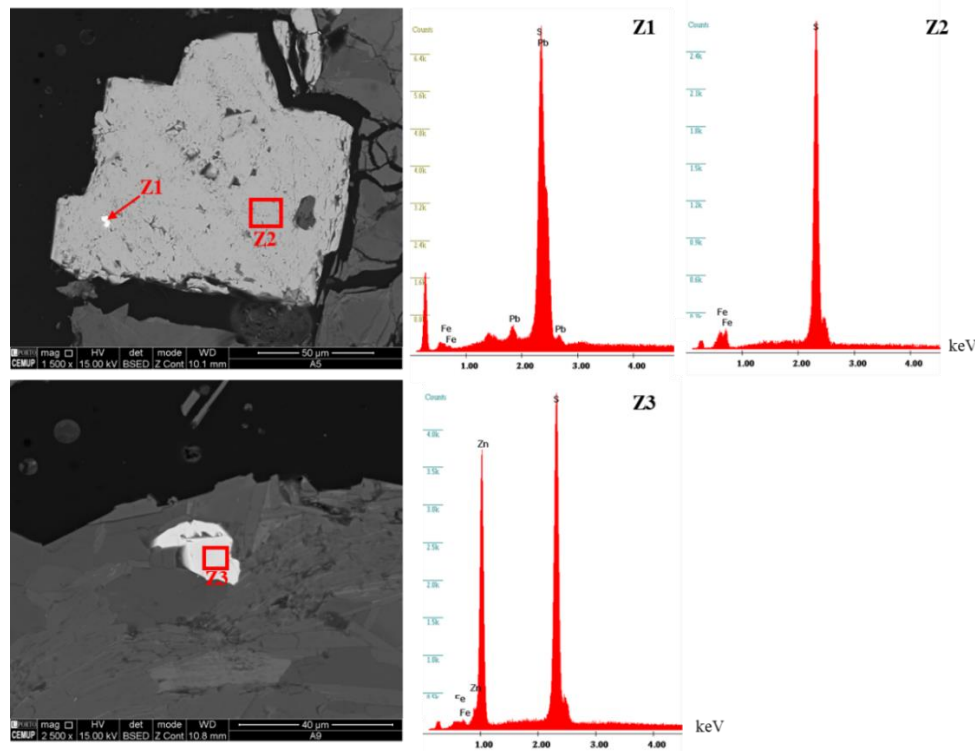


Figure 53 - SEM image and EDX spectra of Pb sulfide (Z1) within Fe sulfides (Z2) in sample A5 and Zn sulfide (Z3) in sample A9.

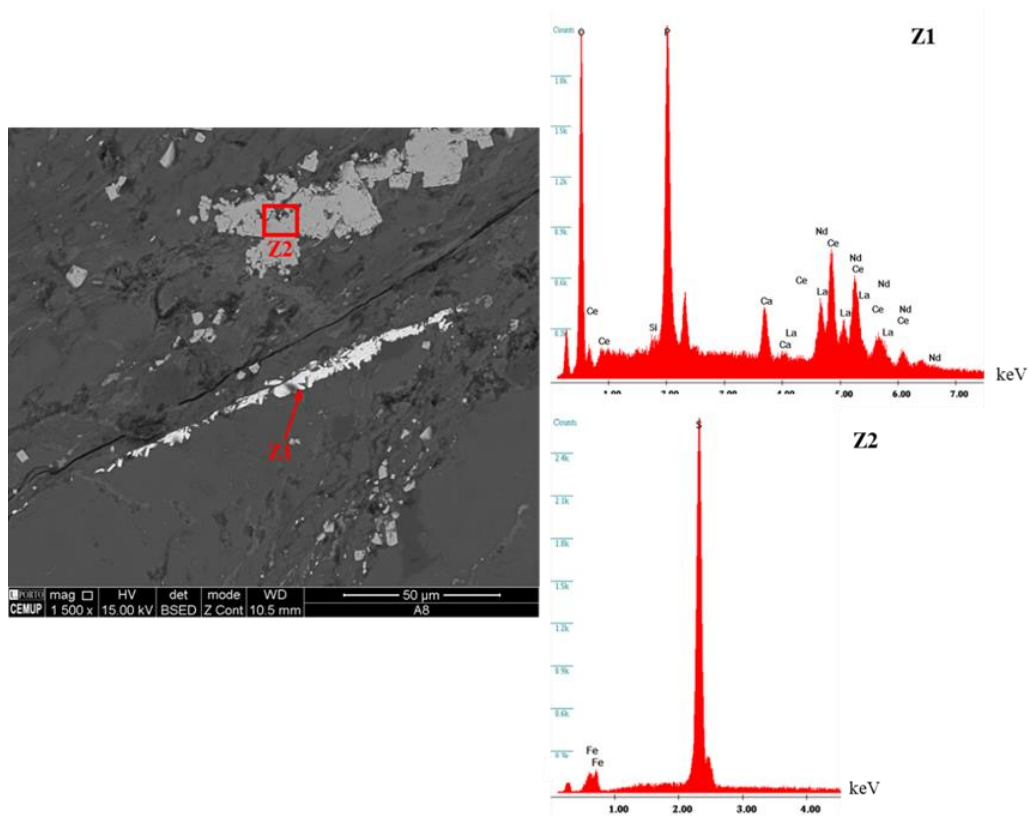


Figure 54 - SEM image and EDX spectra of particles of REE phosphates (Z1) and Fe sulfides (Z2) in sample A8.

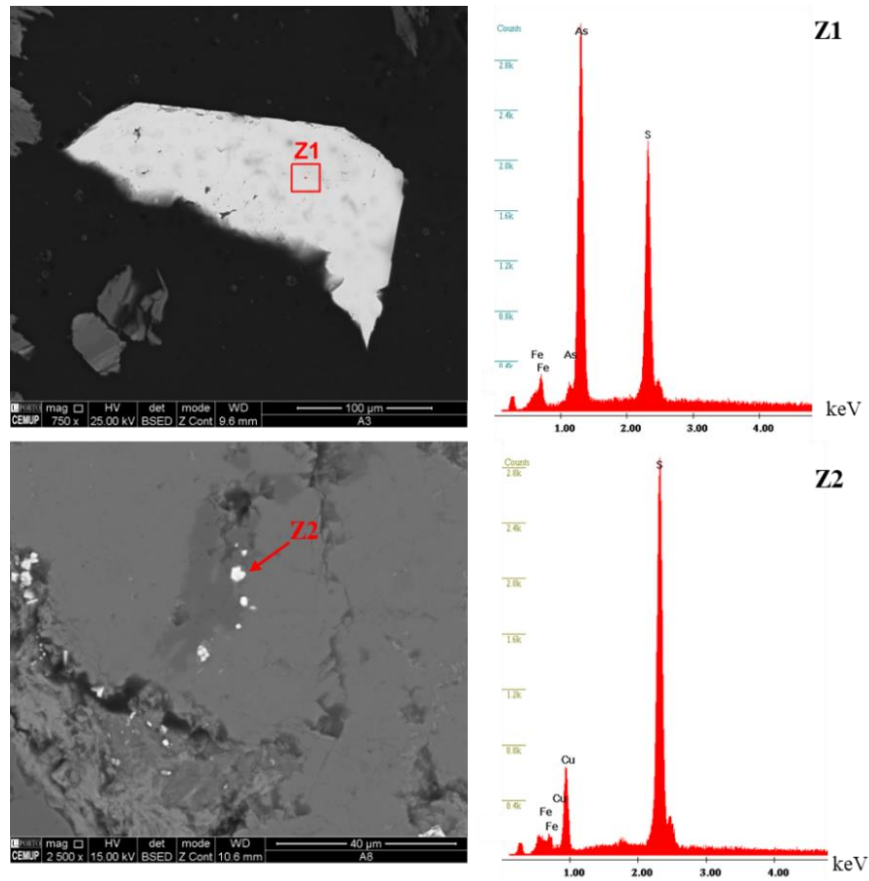


Figure 55 - SEM image and EDX spectra of arsenopyrite (Z1) in sample A3 and chalcopyrite (Z2) in sample A8.

4.3.2. Maturation and paleotemperature

Table 18 shows the obtained values for mean and maximum random reflectance measurements, the number of measured particles and standard deviation of the studied samples. In samples A5, A8, and A14 the observed organic particles were very small, and the measurement of reflectance was not possible. The vitrinite-like particles present a mean random reflectance (R_r) of 2.24% and 3.04% for outcrop samples, for the drill core samples far from skarns ($n = 9$) ranges from 2.41% to 3.84%, and for the drill core samples near the skarns ($n = 2$) is 3.23% and 3.67%. The maximum random reflectance (R_{max}) is 3.26% and 5.70% for the outcrop samples, varies from 3.86% to 6.45% in samples from drill cores far from skarns, and between 6.33% and 6.53% in samples near skarns. Generally, the reflectance values of samples from both outcrop and drill cores are in a similar range (Table 18).

Table 18 - Number of measured organic particles (N), mean (Rr) and maximum random reflectance (R_{max}), standard deviation (SD) and estimated paleotemperatures based on the Rr of the studied samples.

	Sample	Depth (m)	N	Rr (%)	SD	R _{max} (%)	SD	Paleotemperature ¹ (°C)	
Outcrop	A1	-	3	3.04	0.69	5.70	1.47	294	
	A2	-	1	2.24	-	3.26	-	255	
Boreholes	RGD 039	A4	34.0	2	2.83	0.81	5.06	1.88	285
		A3	41.0	15	2.41	0.47	3.86	0.89	265
	RGD 034	A6	51.2	6	3.52	0.94	6.45	2.20	313
		A5*	90.0	-	-	-	-	-	-
		A7	123	3	3.84	0.41	5.06	0.44	324
	RGD 038	A9*	28.2	3	3.67	0.56	6.53	1.32	318
		A8	41.5	-	-	-	-	-	-
	RGD 040	A10*	89.8	1	3.23	-	6.33	-	302
		A11	111	4	3.31	0.42	6.02	0.93	305
		A12	156	1	3.71	-	5.51	-	320
	RGD 035	A13	96.0	7	2.78	1.09	4.32	1.81	283
		A14*	159	-	-	-	-	-	-
		A15	186	3	3.06	0.28	5.15	0.59	295

*Samples near skarns; ¹T_{max} = (lnRr + 1.19)/0.00782 (Barker and Pawlewicz,1994).

Figure 56 displays the values of mean and maximum random reflectance determined for the samples, as well as the fields for classification of OM maturation (anthracite, meta-anthracite, and semi-graphite) proposed by Kwiecinska and Petersen (2004) based on the R_{max} values. These authors suggested that the classification would be anthracite, when R_{max} is between 2.0% and 5.0 %; meta-anthracite, when R_{max} ranges from 5.0% to 6.5%; and semi-graphite when R_{max} is between 6.5% and 9.0%.

Samples from outcrops correspond to meta-anthracite and anthracite for A1 and A2, respectively. Regarding to the samples from the drill cores, the maturation of the OM ranges from anthracite to meta-anthracite in samples far from skarns (Fig. 56, blue bars), and semi-graphite and meta-anthracite in samples located near skarns, thus evidencing higher maturation (Fig. 56, red bars).

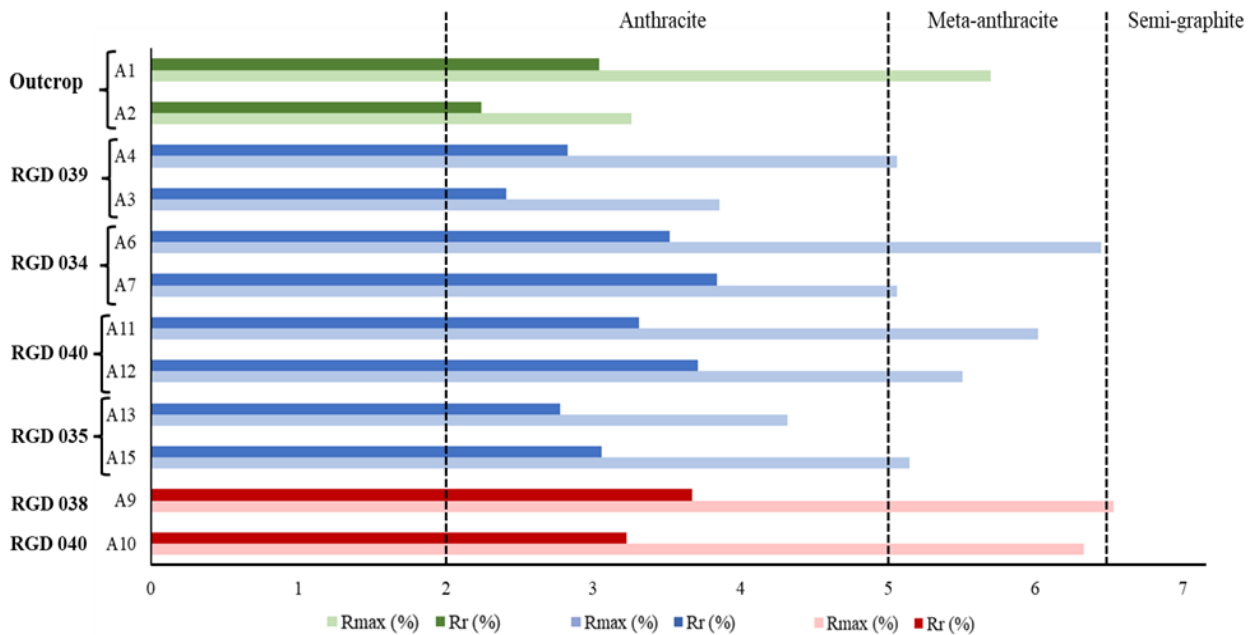


Figure 56 - Mean and maximum random reflectance of the OM in outcrop samples (green), drill core samples far from skarns (blue) and drill core samples near skarns (red). Fields anthracite, meta-anthracite and semi-graphite based on $R_{\max}$ values.

The paleotemperatures can be estimated based on the reflectance of the OM, using the equation proposed by Barker and Pawlewicz (1994), $T_{\max} = (\ln R_r + 1.19)/0.00782$, being $T_{\max}$ the maximum temperature. Table 18 presents the maximum temperatures estimated for the studied samples, considering the mean random reflectance (Rr) measured in the vitrinite-like particles.

The outcrop samples show values of paleotemperature of 255°C and 294°C, whereas the values of maximum temperatures vary between 265°C and 324°C in samples far from skarns, and between 302°C and 318°C in samples near skarns (Table 18).

The contact metamorphism and metasomatic processes, resulting from infiltration of magmatic-, metamorphic- and meteoric-derived fluids, related to the formation of skarns, as described in the literature (e.g., Martinez et al., 1988; Meinert, 1992; Meinert et al., 2005), may have affected the maturation of the OM in the black shales and caused its variability. The circulation of hydrothermal fluids in black shales can condition their composition and consequently the mineralized structures. Other studies stated that post-depositional diagenetic and metamorphic processes have an impact on the mineralogy of black shale and the distribution of trace elements (e.g., Rimstidt et al., 2017).

The proximity to the granitic body also justifies the variability amongst the samples from the different drill cores. Samples from RGD 034 and RGD 040 have higher maturation, being these the deepest drill cores (≈ 120 m to 160 m depth) and, in the case of RGD 034, the closest to the contact with granite. Samples RGD 038 and RGD 039 reached depths around 40 m, and RGD 35 is the furthest from the granitic body; samples from these drill cores have generally lowest maturation. The local proximity to skarns explains the higher maturation of OM in samples A9 and A10 at about 28 m and 90 m depth, respectively.

4.3.3. Geochemical composition of black shales

Tables 19 and 20 present the geochemical composition of major and trace elements of the studied samples, together with TOC and total sulfur (TS) data. The TOC is 0.74% and 0.85% for the outcrop samples and varies between 0.02% and 0.67% for drill core samples, except for sample A3 that have a TOC value of 3.42% (Table 19). These lower TOC values justify the difficulty to identify organic particles under the microscope in the studied samples. The TS values are, in general, lower than 1%, with exception for A4, A6, A8, A9 and A11 that present values $>1\%$ (Table 19).

From the determined major elements, the most abundant in the studied samples are Al, Fe, and K, followed by minor concentrations of Ca, Mg, Na, P and Ti. This geochemical composition (Table 19) is coherent with the mineralogy identified through microscopic observations and also the macroscopic information from logging.

Table 19 - TOC (%), TS (%), and concentration of major (wt. %) and trace elements (ppm) in the studied samples.

	Outcrop		RGD 039		RGD 034			RGD 038		RGD 040			RGD 035		
	A1	A2	A4	A3	A6	A5*	A7	A9*	A8	A10*	A11	A12	A13	A14*	A15
TOC	0.85	0.74	0.17	3.42	0.35	0.03	0.09	0.12	0.30	0.05	0.67	0.50	0.47	0.02	0.43
TS	0.02	< 0.01	1.10	0.05	1.32	0.29	0.11	2.57	2.03	0.78	1.29	0.40	0.67	0.02	0.48
Al	6.82	7.64	7.81	9.65	7.25	7.16	7.42	7.39	8.05	8.15	7.37	7.03	8.95	8.54	6.83
Ca	0.39	0.99	0.89	0.44	0.23	4.96	0.44	0.40	0.26	1.33	0.31	0.20	2.01	0.18	0.30
Fe	2.07	3.18	5.75	5.95	4.71	6.12	3.99	5.86	5.55	4.32	5.43	3.08	6.04	4.77	2.97
K	3.08	3.09	2.79	4.94	3.56	0.94	3.09	3.90	5.83	2.59	3.45	3.08	2.62	2.92	3.60
Mg	0.88	0.85	1.41	1.90	1.03	3.99	1.20	1.43	1.43	1.57	1.19	1.03	1.41	1.69	1.47
Na	1.00	0.61	1.35	0.77	1.31	0.37	0.93	0.73	0.17	1.96	1.25	1.53	2.13	3.72	0.83
P	0.02	0.43	0.06	0.05	0.05	0.04	0.06	0.05	0.05	0.06	0.05	0.06	0.06	0.07	0.06
Ti	0.31	0.40	0.40	0.70	0.28	0.28	0.40	0.40	0.47	0.37	0.23	0.28	0.43	0.32	0.29
Ag	0.02	0.11	0.10	0.49	0.18	0.05	0.05	0.20	0.39	0.12	0.16	0.15	0.10	0.04	0.10
As	73.5	124	12.2	179	5.90	238	34.6	249	37.2	27.7	2.30	3.30	148	109	22.5
Ba	583	651	428	954	417	353	660	302	222	497	297	535	530	670	537
Be	4.00	4.00	1.00	7.00	3.00	15.0	3.00	5.00	4.00	3.00	3.00	3.00	3.00	6.00	3.00
Bi	0.70	0.90	0.44	3.10	0.51	1.10	0.46	0.80	1.28	0.39	0.43	0.31	0.67	0.63	0.29
Cd	<0.02	<0.02	0.36	1.29	0.72	0.45	<0.02	0.32	<0.02	0.20	0.44	0.03	0.10	<0.02	0.85
Co	3.00	12.4	27.8	16.3	18.0	3.90	13.3	30.5	18.4	16.0	22.7	12.3	43.7	21.7	17.4
Cr	91.0	100	112	194	81.0	93.0	95.0	81.0	216	90.0	85.0	75.0	97.0	96.0	79.0
Cs	57.7	53.2	15.6	66.7	258	175	23.0	140	124	123	262	51.8	346	32.9	69.8
Cu	43.9	44.2	56.3	186	46.8	47.5	25.7	54.9	349	43.3	65.6	44.5	52.7	71.8	35.4
Ga	22.9	23.1	25.3	33.3	22.9	21.9	25.9	24.6	23.8	22.9	22.0	22.2	25.3	25.7	22.9
Hf	3.67	2.81	3.33	7.00	3.18	1.20	3.03	3.15	5.52	3.12	2.84	3.14	2.88	3.43	3.17
In	0.05	0.05	0.08	0.11	0.06	0.07	0.07	0.09	0.04	0.06	0.06	0.05	0.07	0.04	0.08
Li	137	190	138	221	229	361	145	303	165	213	169	141	241	162	130
Mn	195	294	570	451	253	936	437	496	413	615	337	265	507	273	272
Mo	7.73	2.37	0.81	38.7	9.42	0.86	1.21	3.70	5.40	3.11	8.67	13.1	0.88	0.29	5.64
Nb	4.33	10.9	12.4	18.1	3.69	9.00	12.7	12.7	14.3	11.1	2.90	5.60	11.8	9.80	4.49
Ni	11.5	29.1	104	124	72.1	55.1	42.3	82.8	133	53.3	108	59.1	101	58.5	75.6
Pb	21.4	24.1	17.5	44.2	13.5	12.3	18.8	21.5	25.9	24.4	20.6	14.1	23.9	7.59	45.0
Re	<0.002	<0.002	0.010	0.015	0.018	<0.002	<0.002	0.023	0.005	0.003	0.003	0.004	<0.002	<0.002	0.030
Rb	124	115	85.8	172	158	96.1	111	156	322	136	150	119	129	92.8	112
Sb	0.45	0.26	0.12	0.55	0.19	0.40	0.14	0.39	1.11	0.08	0.18	0.25	0.44	0.18	0.29
Sc	12.4	13.5	12.8	21.2	11.4	9.80	12.3	11.4	14.0	13.1	11.9	11.5	15.4	12.5	11.0
Se	1.10	1.10	5.40	<0.30	2.00	0.50	<0.30	3.10	4.70	2.60	2.20	0.40	1.60	0.20	1.50
Sn	3.90	5.50	3.90	16.8	9.20	19.1	4.20	6.80	4.10	3.70	3.20	3.20	3.20	22.4	3.00
Sr	131	150	207	223	80.0	764	118	91.0	112	258	100	91.0	357	336	48
Ta	0.20	0.80	0.80	1.40	0.20	0.60	0.90	1.00	1.10	0.80	0.10	0.30	0.90	0.70	0.20
Te	0.11	0.08	0.03	0.14	0.03	0.43	0.03	0.15	0.13	0.11	0.03	0.06	0.22	0.09	0.05
Tl	0.83	0.90	0.62	1.99	1.03	0.68	0.63	1.20	3.56	1.03	1.03	0.77	1.12	0.80	0.67
Th	12.9	15.2	10.7	21.1	11.7	8.3	10.8	11.2	12.1	10.9	12.2	13.2	12.9	10.4	10.7
U	8.50	6.10	4.20	13.6	8.60	2.60	3.40	4.80	8.60	4.20	5.30	4.00	3.10	3.40	4.20
Y	9.20	67.7	18.8	46.5	8.10	29.7	19.9	18.3	15.7	13.1	8.00	7.10	19.5	5.60	6.40
V	119	148	241	287	109	95	123	208	192	246	135	142	120	129	218
W	5.20	8.30	4.40	9.80	6.30	1.30	4.40	6.80	5.40	2.10	2.90	4.10	1.10	7.00	5.90
Zn	36.0	63.0	136	214	110	92.7	99.9	137	237	133	145	80.1	146	44.6	248
Zr	126	103	111	241	103	32.6	106	99.5	169	95.0	96.7	105	95.1	120	109

*Samples near skarns.

Table 20 - Concentration of REE (ppm) in the studied samples.

	Outcrop		RGD 039		RGD 034			RGD 038		RGD 040			RGD 035		
	A1	A2	A4	A3	A6	A5*	A7	A9*	A8	A10*	A11	A12	A13	A14*	A15
La	20.7	154	31.9	93.7	30.2	30.8	31.6	33.6	32.1	33.8	40.3	37.5	41.6	11.6	26.9
Ce	51.9	317	68.6	205	63.0	66.5	68.6	73.5	73.5	70.3	84.1	79.2	87.7	27.9	58.9
Pr	7.00	46.5	8.50	26.6	7.60	7.90	8.60	9.40	9.40	8.30	10.5	9.70	10.3	3.50	7.00
Nd	28.9	183	33.3	103	31.3	29.6	32.6	36.9	37.2	31.6	40.1	38.9	38.8	15.1	26.5
Sm	6.00	42.4	6.40	19.4	5.10	5.80	6.50	6.70	7.00	5.50	7.90	6.30	7.70	2.50	5.30
Eu	1.20	6.30	1.30	3.50	1.00	1.00	1.10	1.20	1.30	1.00	1.40	0.90	1.10	0.40	0.90
Gd	4.40	31.4	5.50	15.3	4.30	5.40	5.60	5.80	5.00	4.70	5.30	5.30	6.40	2.20	3.10
Tb	0.50	3.90	0.60	2.10	0.50	0.90	0.70	0.80	0.60	0.50	0.50	0.40	0.90	0.20	0.30
Dy	2.90	20.4	3.80	11.2	2.30	5.30	4.20	4.10	3.70	3.30	3.00	2.10	4.10	1.10	2.00
Ho	0.40	2.60	0.80	2.00	0.30	1.10	0.80	0.70	0.70	0.60	0.30	0.30	0.90	0.30	0.30
Er	0.90	6.50	2.10	5.10	0.70	2.80	2.10	2.30	1.50	1.50	0.70	0.80	2.60	0.80	0.80
Tm	0.20	0.80	0.30	0.70	<0.10	0.40	0.30	0.30	0.30	0.20	0.10	0.10	0.30	0.10	0.10
Yb	1.40	5.80	2.20	4.70	0.80	2.20	2.00	1.90	2.60	1.50	1.00	1.00	2.10	1.00	1.00
Lu	0.20	0.60	0.30	0.70	0.10	0.30	0.30	0.30	0.40	0.20	0.10	0.10	0.30	0.20	0.20
Σ REE	127	822	166	494	147	160	165	177	175	163	195	183	205	67.0	133
Σ LREE	115	744	149	448	137	141	148	160	159	149	183	172	186	61.0	125
Σ HREE	12.1	78.3	16.9	45.3	10.0	19.4	17.1	17.4	16.1	13.5	12.4	11.0	18.7	6.30	8.70

*Samples near skarns; REE - rare earth elements; LREE - light REE; HREE - heavy REE.

Figure 57 shows the concentration and distribution pattern of trace elements in the studied samples. The range of reference composition for background of black shales from Ketris and Yudovich (2009) is also represented (BBS min, BBS max). As can be observed in Figure 57, the distribution pattern of the elements in the studied samples is similar, with slight differences between samples far and near skarns.

Relatively to the distribution pattern of samples from drill cores far from skarns, the sample A3 stands out for relatively higher values of Ag, As, Ba, Be, Bi, Cd, Ga, Hf, Mo, Ni, Sc, Sn, Th, U, V and Zr in comparison with other samples (Table 19). In the samples near skarns, stands out the sample A14, with lower values of Ag, Cd, Cs, Mo, Se and Te and, and on the contrary, the sample A5 with higher values of Cs, Mn and Sr (Table 19).

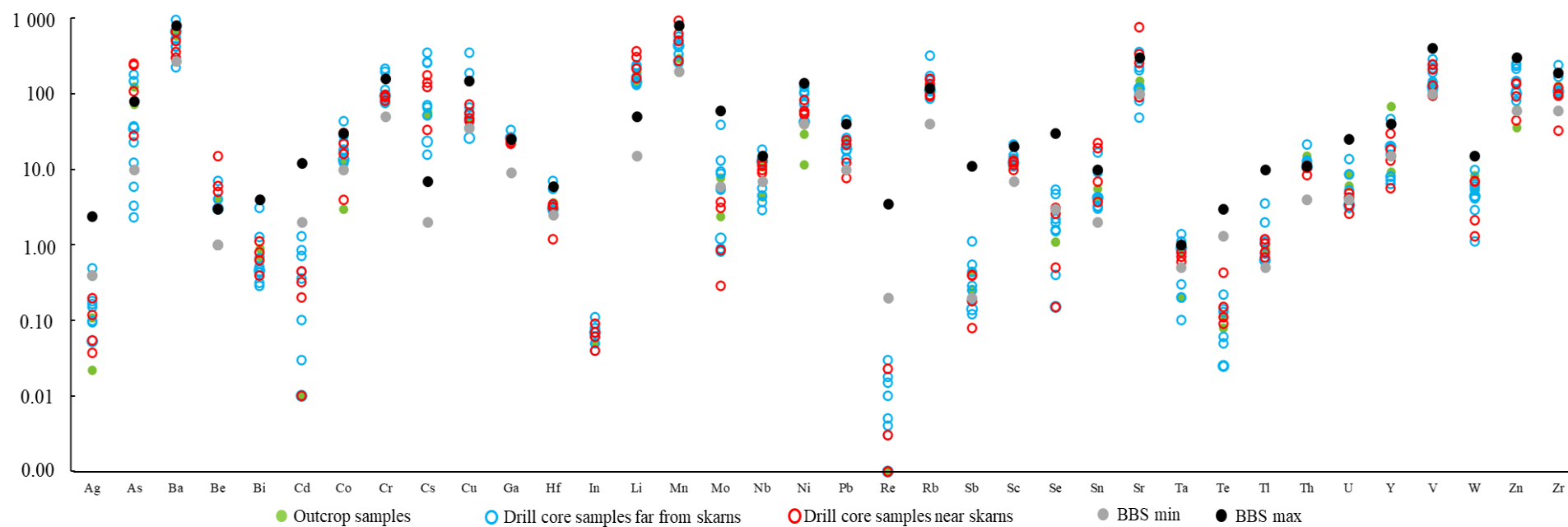


Figure 57 - Concentration of trace elements (ppm) in samples from outcrop and drill cores.

The concentration of rare earth elements (REE) in the studied samples is presented in Table 20. The Σ REE for the outcrop samples is 127 ppm in sample A1 and 822 ppm in samples A2, and varies from 60.7 ppm to 494 ppm, with an average value of 187 ppm in drill core samples (Table 20).

The REE profiles of the black shale samples normalized to BBS (maximum value; Ketris and Yudovich, 2009) and to NASC (Gromet et al., 1984; Taylor and McLennan, 1985; Condie, 1993), presented in Figure 58, are relatively similar, showing flattened profiles. Stands out the negative anomaly of Tm, and the positive anomaly of Pr when considering the BBS. Samples A2 and A3 show a more differentiated and enriched profiles when compared with the other samples, while A6, A8, A11 and A12 have more depleted profiles regarding HREE (Figs. 58A and 58C). Samples near skarns evidence flattened profiles, while sample A14 reveals a more pronounced depleted profile for all REE (Figs. 58B and 58D). Similar to what Boyong et al. (2011) reported, this depletion is frequently remarked in black shales, particularly in well preserved samples, and indicates that this depletion was not severely influenced by the diagenesis and weathering of the rocks.

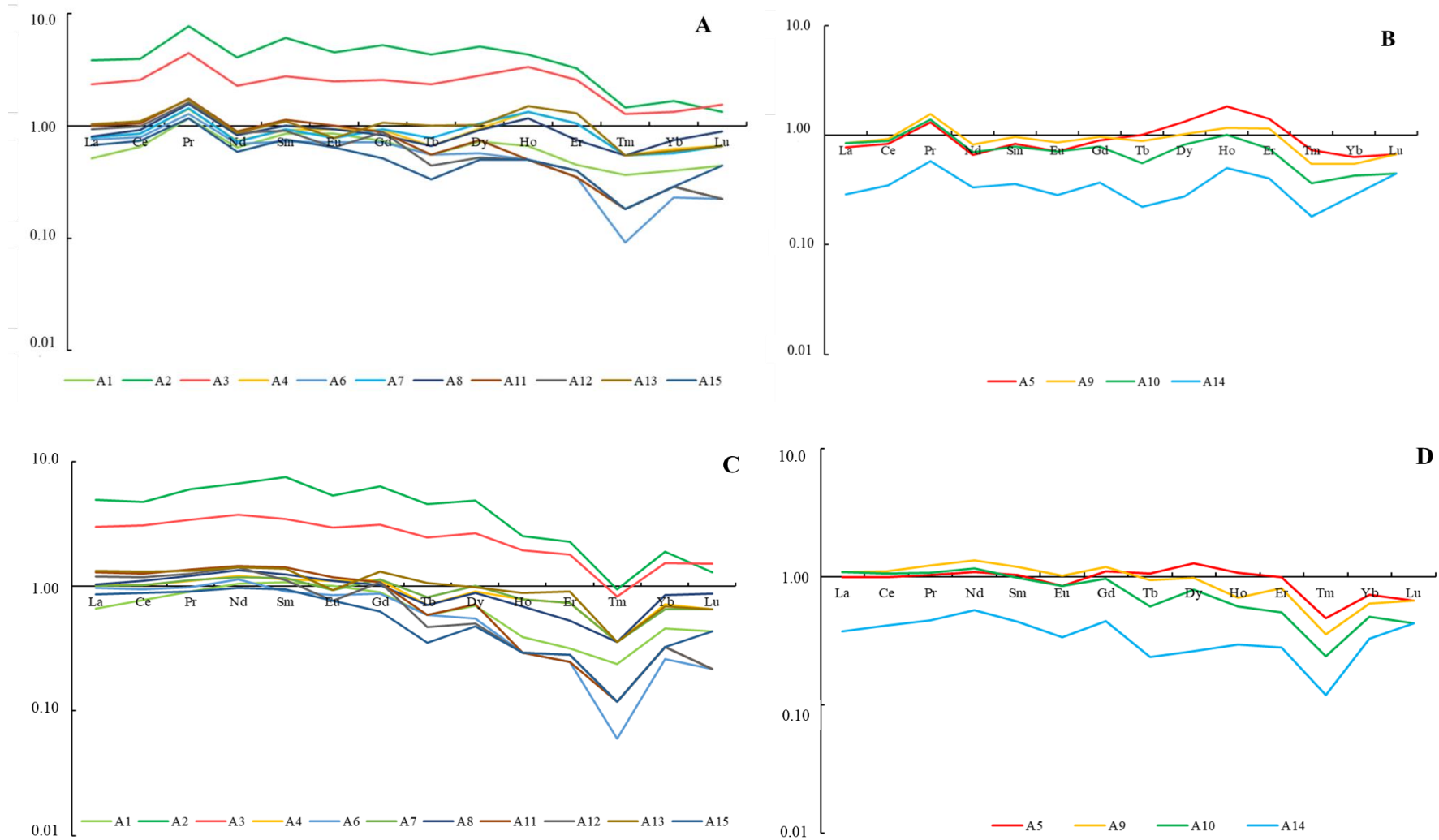


Figure 58 - REE patterns for the studied samples separated considering the proximity to skarns: A) and B) BBS-normalized REE patterns; C) and D) NASC-normalized REE patterns.

4.3.4. Elements distribution and mode of occurrence

Concentration coefficients (CC) were calculated to compare the geochemical composition of samples with reference values, specifically the BBS (Ketris and Yudovich, 2009). Considering the range for BBS, the CC were calculated considering the maximum values. For REE, the CC were calculated considering the sum of LREE and HREE. In Table 21, is presented the group of elements classified, according with Dai et al. (2015, 2016), as: significant enriched $CC > 10$; slightly enriched $2 < CC < 10$ and normal $1 < CC < 2$. Also, according to these authors, $CC < 0.5$ is classified as depleted.

Table 21 - Concentration coefficients (CC) of trace elements in the studied samples relatively to BBS.

Samples		$1 < CC < 2$	$2 < CC < 10$	$CC > 10$
Outcrop	A1	Be, Rb, Th	Cs, Li, LREE, HREE	
	A2	As, Be, Th, Y	Cs, Li	LREE, HREE
Far from skarns	A3	Ba, Cr, Cu, Ga, Hf, Nb, Pb, Rb, Sc, Sn, Ta, Th, Y, Zr	As, Be, Cs, Li	LREE, HREE
	A4	Ga	Cs, Li, LREE, HREE	
	A6	Be, Rb, Th	Li, LREE, HREE	Cs
	A7	Be, Ga	Cs, Li, LREE, HREE	
	A8	Be, Cr, Ta, Th,	Cu, Li, Rb, LREE, HREE	Cs
	A11	Be, Rb, Th	Li, LREE, HREE	Cs
	A12	Be, Th	Cs, Li, LREE, HREE	
	A13	As, Be, Co, Ga, Rb, Sr, Th	Li, LREE, HREE	Cs
	A15	Be, Pb	Cs, Li, LREE, HREE	
	A5	Mn, Sn	As, Be, Li, Sr, LREE, HREE	Cs
Near skarns	A9	Be, Co, Rb, Ta, Th	As, Li, LREE, HREE	Cs
	A10	Be, Rb	Li, LREE, HREE	Cs
	A14	As, Ga, Sr, LREE	Be, Cs, Li, Sn, HREE	

Several elements are depleted or have concentration similar to the reference materials, being slightly depleted ($CC < 1$) to normal ($1 < CC < 2$; Table 21). All samples are slightly enriched ($2 < CC < 10$) to significant enriched ($CC > 10$) in LREE and HREE. This is in accordance with the SEM-EDX analysis, which reveal the presence of minerals with REE and P in some samples (Fig. 54, spectrum Z1). Sample A3 contain the most significant enrichment of trace elements and correspond to the sample with higher value of TOC content (3.42%; Table 19).

Cesium also stands out in all samples, being significant enriched in the majority of samples; the elements As, Be, Cu, Li, Sn, and Sr are slightly enriched in some samples. These elements, as well as REE, are known for their preferential association with silicates, clays, sulfides, and phosphates in rocks with OM (Finkelman et al., 2018). These is consistent with the described mineralogical content of the studied samples.

The enrichment of some elements may be related with the terrigenous sedimentation described for the base of the *Bateiras* Formation (Silva, 2005; Foucaud et al., 2018). However, the enrichment in Cs, Be, Li, and also Rb and Th (Table 21) suggests a contribution of granitic rocks installation and related fluids. This is supported by Noronha et al. (2013) who suggested that granitic magmas played an important role in the thermal evolution of the orogen in CIZ.

The Pearson correlation coefficients were calculated and Table 22 shows the values for selected elements. Positive correlations significant at $p < 0.05$ are identified in blue, while negative correlations significant at $p < 0.05$ are marked in red. The results of Pearson correlation may provide information on the organic and inorganic affinities of elements in rocks with OM (e.g., Grdal, 2008; Bokonda et al., 2019; Betrant et al., 2023). The positive correlation with TOC is indicative of element organic association, while a negative correlation is indicative of element preferential association with mineral matter. The association with mineral matter is normally corroborated by the positive correlation with, for example, Al, Ca, K, Fe, and S, pointing out possible associations with aluminosilicates, carbonates, clays, sulfides, among others.

Table 22 - Pearson correlation coefficients between selected elements.

	TOC	TS	Al	Ca	Fe	K	Mg	P	Ti	Ag	As	Be	Bi	Cd	Cr	Cs	Cu	Li	Mo	Nb	Ni	Pb	Rb	Sc	Sn	Sr	Th	U	W	Zn
TS	-0.21																													
Al	0.54	-0.05																												
Ca	-0.19	-0.22	-0.01																											
Fe	0.09	0.50	0.55	0.37																										
K	0.45	0.49	0.29	-0.69	0.07																									
Mg	-0.03	-0.17	0.10	0.85	0.51	-0.45																								
P	0.03	-0.21	0.00	0.00	-0.28	-0.05	-0.25																							
Ti	0.71	-0.01	0.79	-0.12	0.37	0.54	0.01	-0.20																						
Ag	0.69	0.42	0.53	-0.27	0.41	0.80	-0.02	-0.09	0.72																					
As	0.21	-0.13	0.30	0.53	0.44	-0.18	0.57	0.10	0.37	0.12																				
Be	0.10	-0.29	0.04	0.76	0.34	-0.37	0.90	-0.08	0.03	0.02	0.71																			
Bi	0.86	-0.09	0.65	0.08	0.39	0.45	0.30	0.01	0.84	0.78	0.51	0.42																		
Cd	0.65	0.04	0.24	0.00	0.29	0.24	0.27	-0.23	0.33	0.52	0.14	0.20	0.55																	
Cr	0.53	0.25	0.59	-0.11	0.38	0.71	0.10	-0.05	0.77	0.82	0.10	0.11	0.76	0.22																
Cs	-0.10	0.43	0.11	0.30	0.46	-0.11	0.12	-0.19	-0.19	0.06	0.13	0.07	-0.09	0.12	-0.14															
Cu	0.32	0.45	0.42	-0.18	0.35	0.77	0.05	-0.12	0.55	0.79	0.01	0.07	0.57	0.08	0.93	-0.02														
Li	-0.02	0.12	0.13	0.72	0.60	-0.33	0.70	-0.05	0.08	0.10	0.79	0.73	0.29	0.22	-0.05	0.49	-0.06													
Mo	0.94	-0.10	0.43	-0.27	0.08	0.50	-0.03	-0.15	0.60	0.76	0.09	0.09	0.79	0.70	0.49	-0.09	0.35	-0.02												
Nb	0.35	0.03	0.74	0.09	0.52	0.32	0.20	0.10	0.88	0.52	0.46	0.14	0.64	0.07	0.67	-0.24	0.49	0.22	0.24											
Ni	0.32	0.67	0.52	-0.13	0.73	0.57	0.09	-0.32	0.46	0.72	0.00	-0.10	0.41	0.44	0.62	0.34	0.65	0.07	0.36	0.39										
Pb	0.63	-0.03	0.27	-0.21	-0.08	0.50	-0.10	0.05	0.54	0.52	0.04	-0.14	0.49	0.61	0.41	-0.09	0.29	-0.15	0.55	0.27	0.35									
Rb	0.17	0.63	0.21	-0.27	0.26	0.81	-0.13	-0.13	0.37	0.74	-0.08	-0.09	0.37	0.02	0.75	0.21	0.90	-0.01	0.25	0.29	0.57	0.26								
Sc	0.85	-0.10	0.86	-0.19	0.28	0.50	-0.10	0.06	0.91	0.70	0.20	-0.06	0.82	0.40	0.69	-0.04	0.47	-0.05	0.73	0.67	0.47	0.56	0.30							
Sn	0.23	-0.35	0.38	0.34	0.36	-0.18	0.64	-0.09	0.17	0.10	0.55	0.74	0.49	0.29	0.17	-0.11	0.09	0.45	0.23	0.24	0.00	-0.22	-0.17	0.17						
Sr	-0.11	-0.33	0.22	0.92	0.45	-0.65	0.89	-0.10	-0.02	-0.23	0.57	0.82	0.19	-0.01	-0.01	0.20	-0.09	0.66	-0.19	0.20	-0.08	-0.31	-0.29	-0.06	0.62					
Th	0.93	-0.15	0.57	-0.33	-0.01	0.53	-0.28	0.26	0.74	0.69	0.14	-0.11	0.76	0.43	0.52	-0.10	0.33	-0.12	0.85	0.40	0.27	0.56	0.24	0.87	0.06	-0.27				
U	0.81	0.11	0.35	-0.38	0.02	0.70	-0.21	-0.01	0.61	0.77	0.03	-0.03	0.75	0.52	0.66	-0.07	0.56	-0.08	0.81	0.25	0.31	0.48	0.53	0.68	0.12	-0.33	0.78			
W	0.55	-0.08	0.22	-0.57	-0.18	0.60	-0.33	0.36	0.48	0.47	0.14	-0.09	0.52	0.35	0.36	-0.49	0.27	-0.21	0.52	0.27	0.04	0.36	0.17	0.43	0.29	-0.45	0.61	0.65		
Zn	0.31	0.47	0.27	-0.14	0.36	0.61	0.07	-0.25	0.42	0.66	-0.08	-0.13	0.35	0.57	0.55	0.16	0.57	-0.03	0.35	0.30	0.77	0.76	0.56	0.37	-0.21	-0.23	0.22	0.31	0.10	
REE	0.50	-0.20	0.27	0.01	-0.09	0.16	-0.16	0.86	0.46	0.30	0.26	0.03	0.46	0.12	0.25	-0.15	0.08	0.06	0.32	0.34	-0.07	0.34	0.02	0.47	0.00	-0.08	0.66	0.37	0.50	-0.03

Positive correlations significant at p<0.05 in blue; negative correlations significant at p<0.05 marked in red.

The results reveal a significant positive correlation coefficient between TOC and Ti, Ag, Bi, Cd, Mo, Sc, Th, and U ($r \geq 0.65$; $p < 0.05$; Table 22), indicating that are partially organically bonded. The correlation between OM and some of these elements has been identified in other studies (e.g., Ross and Bustin, 2009; El-Anwar et al., 2018; Finkelman et al., 2018; Laranjeira et al., 2023).

The negative weak correlation between TOC and S indicated that S is preferentially associated with inorganic matter, most probably with sulfides, since S correlates positively with Fe, Cu, Ni, and Zn. The positive correlations between Fe and Zn, S and Zn, and Cd and Zn ($r=0.57$, $p<0.05$) indicate the presence of sphalerite. Sphalerite hosting Cd and Zn in black shales has already been described (e.g., Perkins and Foster, 2004; Tuttle et al., 2009; Perkins and Mason, 2015). The occurrence of sphalerite in the studied samples was pointed out based on SEM-EDX analysis (Fig. 53, spectrum Z3).

The significant positive correlation ($r=0.86$, $p<0.05$) between REE and P supports their association in phosphates. The significant positive correlation ($r>0.75$, $p<0.05$) between Al and Fe, Ti, Ag, Bi, Cr, Nb, Ni, Sc and Th reveals their association with aluminosilicates. It is also possible to observe a strong positive correlation between Ca and Mg and Sr ($r\geq 0.85$, $p<0.05$; Table 22), revealing their carbonate association.

The intercorrelation analysis between TS and Ca considering some elements is represented in Figure 59. The preferential association of elements with sulfides and carbonates can be depicted.

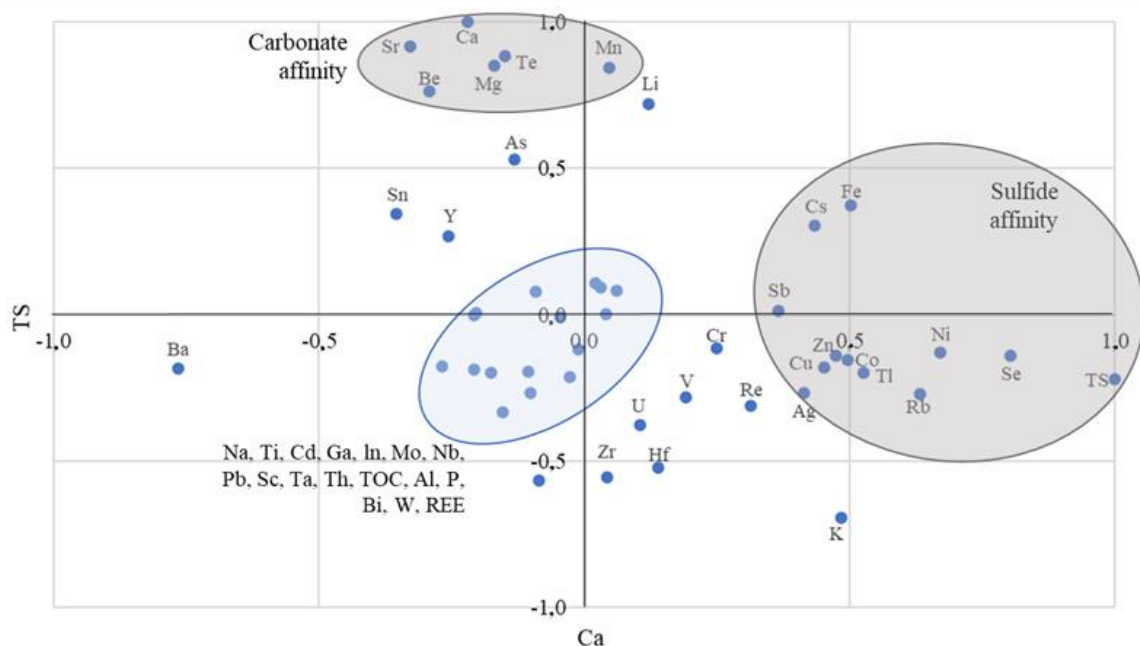


Figure 59 - Cross-plot correlation of the Pearson correlation coefficients of elements versus TS and Ca.

4.3.5. Paleo-redox environment conditions

The variation of some trace elements, such as Co, Cr, Mo, Ni, Th, U and V, can be useful to the interpretation of paleo-redox conditions (e.g., Jones and Manning, 1994; Lyons et al., 2003; Tribovillard et al., 2006; Reinhard et al., 2013). Tribovillard et al. (2006) suggested that there is a predisposition to authigenic enrichment of these sensitive trace elements in oxygen depleted environments due to their less solubility under reducing conditions compared to oxidizing conditions. Some ratios, such as Ni/Co and V/Cr, can be used to infer paleoenvironment conditions (e.g., Jones and Manning, 1994; Tribovillard et al., 2006; Lin et al., 2019).

Considering the ratio Ni/Co, Jones and Manning (1994) suggest that values <5 are relative to oxic conditions, between 5 and 7 infer suboxic conditions, and values >7 indicate anoxic conditions. As for V/Cr, values <2 refer to oxic conditions, and values above 2 indicate anoxic conditions (Jones and Manning, 1994). Figure 60 shows that the studied black shale samples are associated, principally with oxic conditions, but some exhibit tendency for anoxic conditions (samples A3, A8, and A5 considering Ni/Co; samples A4, A9, A10 and A14 considering V/Cr). This is consistent with the low TOC content of the studied samples, since preservation of OM is favored under reducing conditions. The formation of black shales in oxic conditions has been described in other studies (Reynaud et al., 2018).

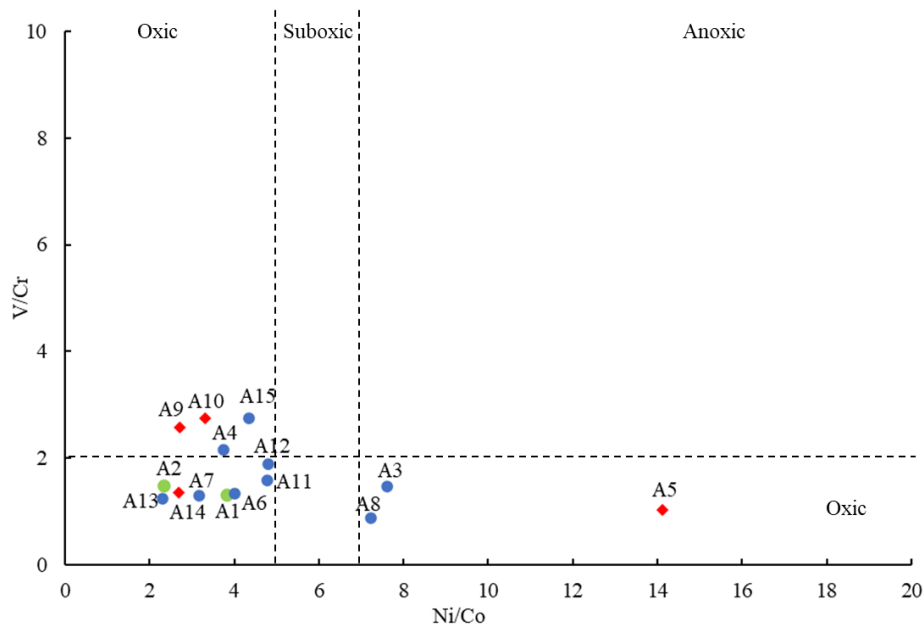


Figure 60 - Cross-plot of redox sensitive element ratios V/Cr and Ni/Co. The V/Cr and Ni/Co boundaries proposed by Jones and Manning (1994).

Some authors (e.g., Galarraga et al. 2008; El-Anwar et al. 2018) proposed that V/Ni ratio >3 can indicate deposition under marine reducing conditions, while values between 1.9 and 3 implies suboxic environment conditions with mixed terrigenous and marine source of material, and ratio <1.9 indicates predominantly terrigenous material. Samples A1 (10.4), A2 (5.09) and A10 (4.62) have values of V/Ni ratio above 3, indicating marine reducing conditions; samples A3 (2.32), A4 (2.32), A7 (2.91), A9 (2.51), A12 (2.40), A14 (2.21) and A15 (2.88) present values that indicate suboxic environment, with mixed terrigenous and marine source of materials. For samples A5 (1.72), A6 (1.51), A8 (1.44), A11 (1.25) and A13 (1.19), the V/Ni <1.9 reveal a terrigenous origin of materials. This is consistent with Foucaud et al. (2018) that described a terrigenous component in black shales from *Bateiras* Formation in Tabuaço deposit.

4.4. Conclusions

Black shales from *Bateiras* Formation were studied through petrographic, mineralogical, and geochemical analysis in order to characterize these rocks, spatially associated with W-Skarn deposit from DSB.

The petrographic characterization allowed the identification of vitrine-like particles in all samples, although very scarce. Some organic particles exhibit graphitic features in some samples. From the petrographic observations and SEM-EDX analysis, the inorganic matter is mainly composed of aluminosilicates, silicates, Fe and Ti oxides, sulfides, and phosphates in association with REE.

Considering the reflectance of organic particles, the thermal maturation of the studied samples ranges between anthracite and meta-anthracite, and paleotemperatures between 255°C to 324°C were estimated. The variation observed in OM maturation indicate the differentiated effect by metamorphic/metasomatic processes associated with skarns formation in the area, locally in samples from drill cores collected near skarns, and regionally considering the proximity to the granitic body.

Based on the geochemical characterization and considering the CC based on BBS, the enrichment in REE and Cs is the most notorious followed by the enrichment in As, Be, and Li, possibly associated with the contribution of granitic rocks installation and related fluids.

The integration of results with the Pearson correlation coefficients stands out the organic affinity of some elements, the association of TS with mineral matter, preferentially with sulfides. The association of elements with aluminosilicates, carbonates and phosphates

was also identified. The redox sensitive ratios Ni/Co and V/Cr revealed the prevalence of oxic conditions but a tendency to anoxic conditions was also predicted to some samples.

The comprehensive characterization of the black shales from *Bateiras* Formation spatially associated with Vila Seca-Santo Adrião deposit do not reveal significant evidence about their influence in the mineralizing process. However, the studied black shales present evidences of the effect of metamorphic/metasomatic processes related with skarn formation in the thermal maturation of OM. The circulation of hydrothermal fluids in black shales can condition their composition and consequently the mineralized structures.

CHAPTER 5

GENERAL
CONCLUSIONS

The petrographic, mineralogical, and geochemical characterization of black shales from OMZ and CIZ representing different stratigraphic levels and spatially associated with metal deposits was presented. The obtained results represent a contribution to the scientific knowledge about the characteristics of black shales and their role in ore forming processes through a multi-technique approach to characterize the organic and inorganic matter present in these black shales. The results obtained were divided into three chapters according with the age and location of the studied black shales. The general conclusions are presented below considering the different case studies.

Precambrian black shales from OMZ

- The petrographic observations demonstrate the presence of organic particles small, thin and elongated in all samples, with some particles exhibiting graphitic features. It was also possible to observe acritarch remains. The mineral matter is essentially composed of phyllosilicates, quartz and iron oxides.
- The OM maturation indicates the presence of organic particles classified as anthracite to semi-graphite, with paleotemperatures above 300°C, accompanying the burial in the basin and metamorphic/metasomatic processes.
- The concentration and distribution pattern of elements are similar in all samples and correspond to the patterns expected for black shales. An enrichment ($CC > 10$) was observed for Ag, As, Bi, and Se in some samples. The trace elements with organic affinity are Ag, Bi, Cd, Cu, Mo, Ni, Pb, Se, Sr, Te, U, and Y; their moderate affinity indicates an association between OM and sulfides. A sulfide fraction is represented by the association of Ag, Cd, Cu, Pb, and Se.
- The geochemical discriminant diagrams indicated a clastic source with acidic to mixed felsic/mafic signatures related, essentially, with the erosion of the Cadomian Continental Arc developed in the North Gondwana margin, corroborating previous research.
- The paleoredox ratios together with the Ce and Eu anomalies indicate oxic to anoxic paleoenvironmental conditions. The samples that correspond to the anoxic conditions are the samples with higher TOC values, and also have an enrichment in Ag, As, Bi, Co, Cu, Mo, Sb and Se.
- The results indicate that the black shales and the ore occurrences in the studied area appears to be correlated and may represent an important source of metals, as proposed by other authors.

Silurian black shales from OMZ

- Petrographic analysis demonstrated the presence of vitrinite-like particles in all samples, some exhibiting graphitic features, indicative of high maturation. Fragments of graptolites were also observed in some samples, showing an elongated rectangular shape and segmentation. Detrital derived minerals occur on association with OM, iron oxides and sulfides.
- The XRD analysis revealed quartz, plagioclase and muscovite as major mineral phases, together with chlorite, siderite, rutile, arsenopyrite, pyrite and malachite.
- Reflectance measurements classified the samples between the rank stage of anthracite to semi-graphite. For samples near mineralization higher values of paleotemperatures ($> 300^{\circ}\text{C}$) were estimated, indicating that thermal maturation is related to hydrothermal fluids. In drill core samples was observed irregular maturation profiles that could be related to irregular heat distribution due to the circulation of hydrothermal fluids. The higher maturation is explained by the relatively proximity to the mineralizing veins.
- Distribution pattern of elements showed some differences between the samples, standing out the samples of outcrops near mineralizations and some samples from Miguel Vacas deposit that present higher concentrations of Cu and Mn.
- The CC and Pearson correlation coefficients showed the enrichment in Cu in outcrop samples located near the Mociços Cu deposit, whereas in drill cores samples was observed the enrichment of Ag, As, Cu, V, and REE. Sulfur has a positive correlation with TOC indicating that can be organically bound, and a weak positive correlation with Fe, Co, Cr, Cu, Pb and Sb, suggesting that S can also have a partial inorganic affinity.
- Paleoredox conditions determined in the basis of ratios Ni/Co, V/Cr and Th/U indicate deposition in suboxic to anoxic conditions. Considering the results obtained, it was possible to infer: (i) the identification of the supergene enrichment zone around 35 to 50 m depth, with enrichment in Fe, As, Cr, Cu, Ni, U, V and REE, together with highest TOC and S values, indicate that black shales were enriched in metals during post-depositional processes; (ii) the identification of a regional thermal evolution that could be correlated to hydrothermal metamorphism, probably associated with the deep-seated magmatic body, which was previously suggested by other authors.

Cambrian black shales from CIZ

- Despite difficulties in distinguish OM due to scarcity and size, it was possible to observe vitrinite-like particles in all samples, some of them presenting graphitic structure. The mineral matter includes quartz and phyllosilicates, with some iron oxides and sulfides. The maturation of the OM ranges from anthracite to meta-anthracite.
- Through the CC, was identified a significant enrichment in As, Be, Cs, Li and REE, that could be associated with the contribution of granitic rocks installation and related fluids.
- The Pearson correlation coefficients, complemented by SEM-EDX analysis, allow the identification of elements affinity with aluminosilicates, sulfides, carbonates and phosphates.
- The paleo-redox ratios allowed to infer that samples are deposited under more oxidizing conditions, with some samples with tendency to anoxic conditions. The analysis of the samples does not reveal clear evidence about their association in the mineralizing process, but demonstrated that metamorphic/metasomatic processes related with skarn formation affected the maturation of the OM.

The multi-analytical approach comprising the petrographic, mineralogical, and geochemical methods proved to be efficient in the characterization of the organic and inorganic fractions of the studied black shales. It allowed the achievement of contributions on the knowledge about the association of black shales and related metal ore deposits. Moreover, this research represents a contribution to the scientific knowledge about the geology of Portugal, particularly related with black shales occurrences. Petrographic analysis proved to be an essential tool in the study of organic matter dispersed in black shales, providing information about maturation and paleotemperatures.

The determination of the role of the black shales in the ore-forming processes, with emphasis on the OM, was particularly limited in black shales from CIZ, principally due the lower carbon content and organic particles scarcity.

The outcomes from this research may motivate future investigations on this topic. Future work could focus on the petrographic analysis of organic concentrates, the geochemical analysis of organic molecular compounds, and the determination of stable isotopes may be useful for the study of biochemical precursors, provenance, and depositional environment.

CHAPTER 6

PETROGRAPHIC ATLAS

The aim of this petrographic atlas is to present microscopic aspects and mosaics of the studied black shale samples besides those presented in the results, complementing the petrographic analysis.

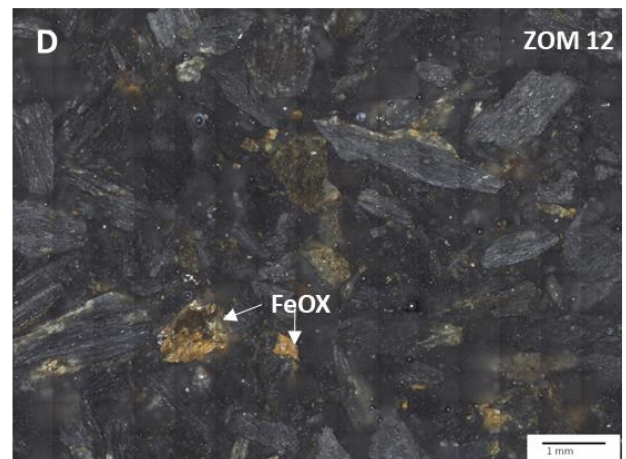
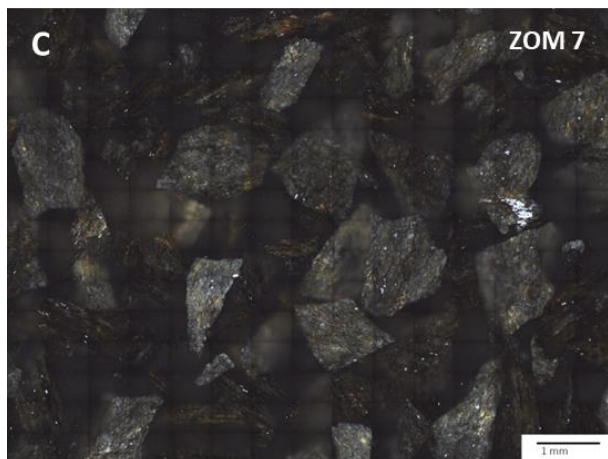
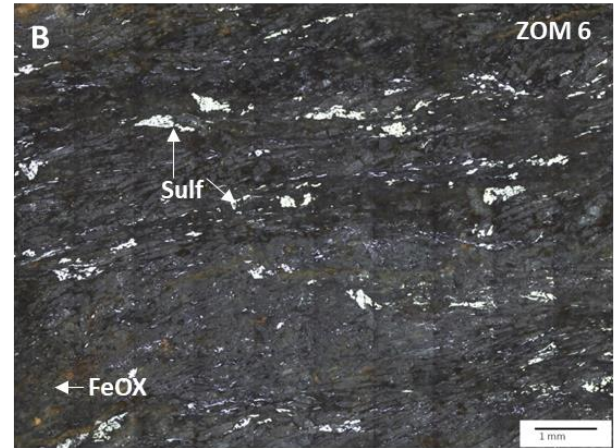
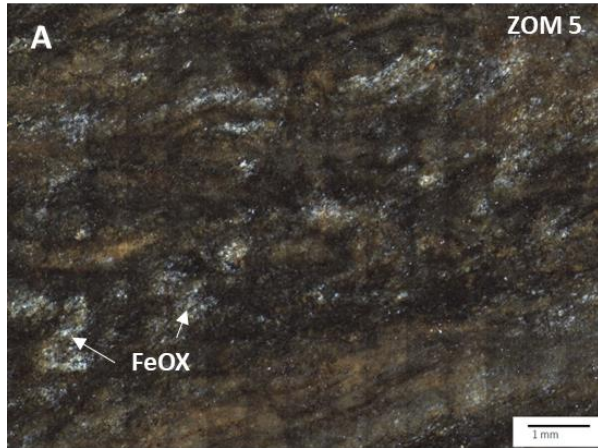
This chapter includes three subchapters. The first correspond to the main aspects observed in black shales samples from Precambrian from OMZ; the second part is related to samples from Silurian from OMZ; and, finally, the last section refers to the general aspects visualized in black shales samples from Cambrian from CIZ.

The petrographic photomicrographs were taken under reflected white light using a Leica 4000 M microscope equipped with a Discus-Fossil system, with the 50x immersion oil objective at Department of Geosciences, Environment and Spatial Planning of Faculty of Sciences from University of Porto.

Mosaics were made by assembling photomicrographs obtained from the successive sweeping with simultaneous acquisition of photomicrographs along the surface of the polished blocks, using the 20x immersion oil objective, for each prepared block (crushed sample and solid piece). The obtained mosaics in this study have 30 to 200 photomicrographs.

6.1. Precambrian black shales from Ossa-Morena Zone

Mosaics



6.1. A – General view of a sample with more siliceous character, showing some iron oxides particles (FeOX; polished blocks of rock pieces).

6.1. B – Petrographic general view of occurrence of iron oxides (FeOX) and sulfides (Sulf; polished blocks of rock pieces).

6.1. C – General view of occurrence sample ZOM 7 (polished blocks of crushed sample).

6.1. D – Petrographic general view of occurrence of iron oxides (FeOX; polished blocks of crushed sample).

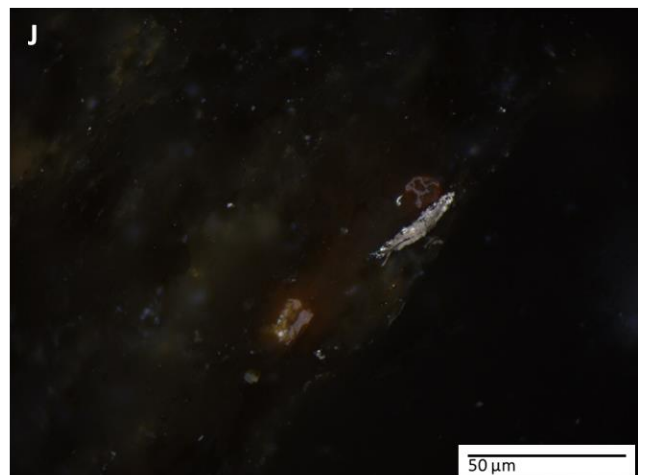
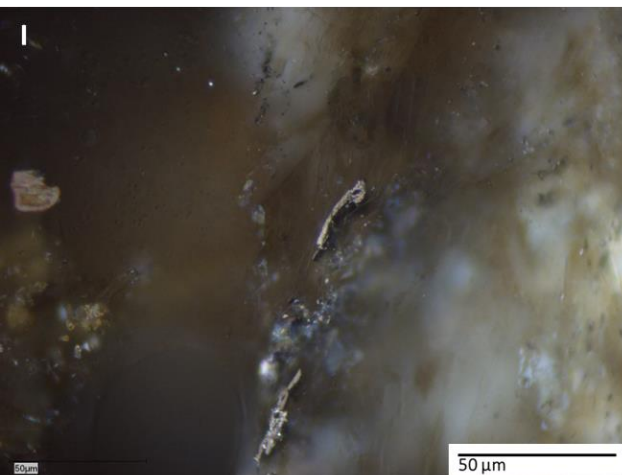
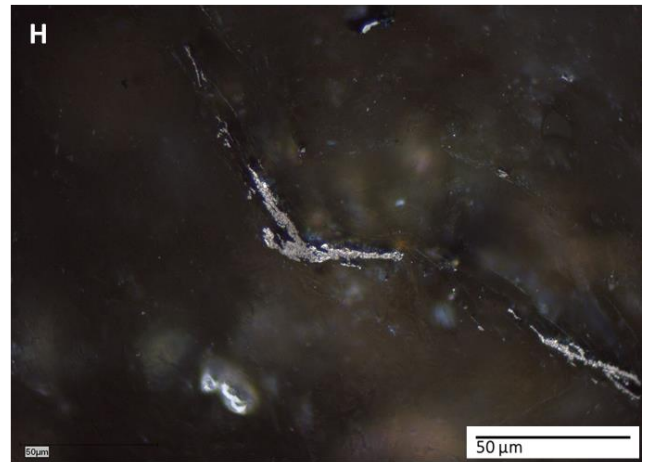
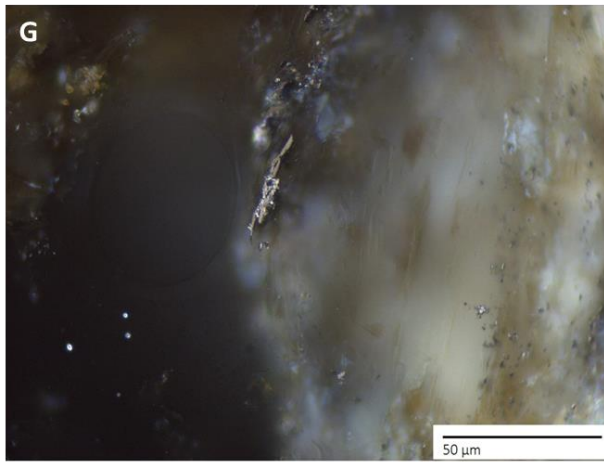
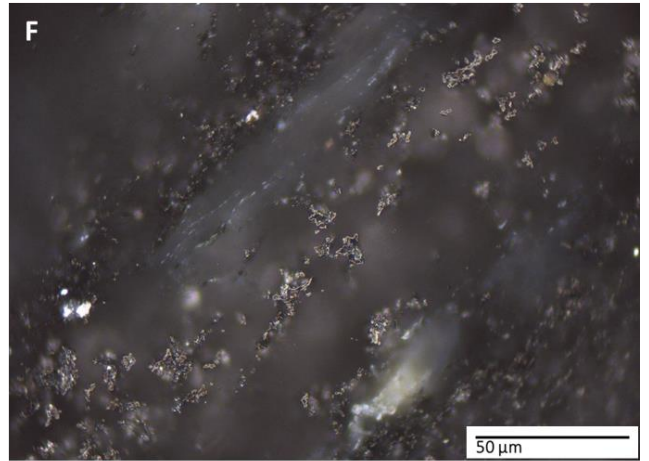
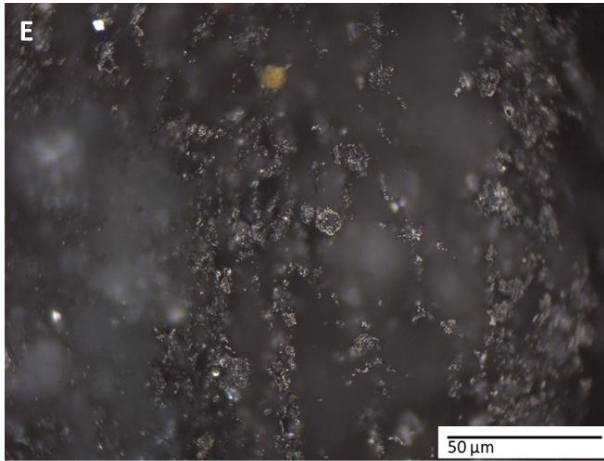
Petrographic aspects

6.1. E and F – Small organic particles, sometimes with rounded shapes, which can be acritarch remains, occurring along vitrinite-like particles and some iron oxides.

6.1. G – Small vitrinite-like particle exhibiting graphitic structure occurring as single flakes.

6.1. H and I – Elongated vitrinite-like particles with graphitic characteristics occurring along mineral matter.

6.1. J – Vitrinite-like particles thin and elongated.



6.2. Silurian black shales from Ossa-Morena Zone

Mosaics

6.2. A – Petrographic general view of occurrence of sulfides (Sulf) and iron oxides (FeOX; polished blocks of rock pieces).

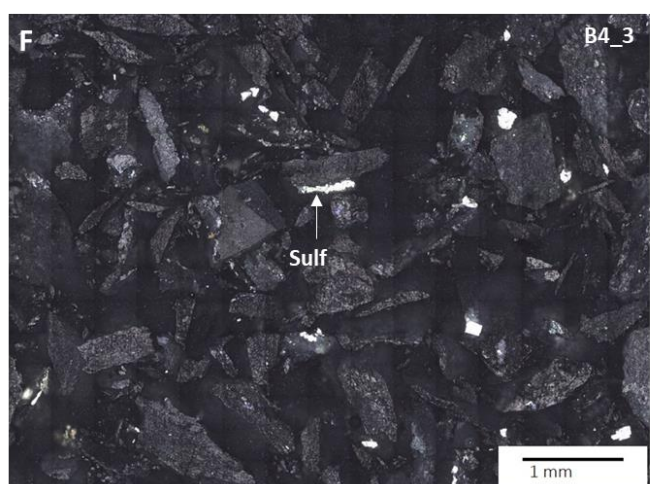
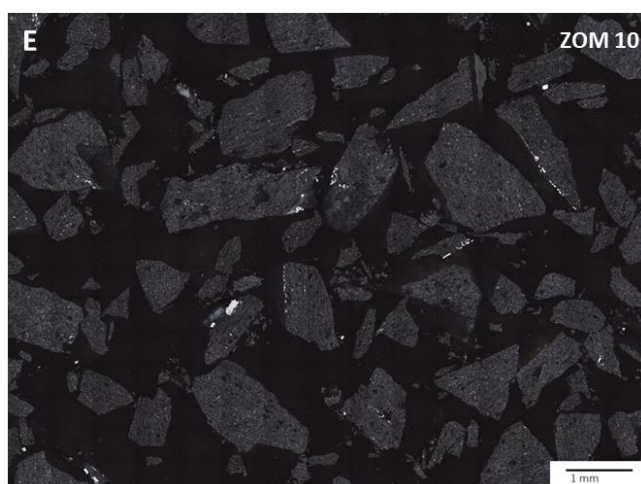
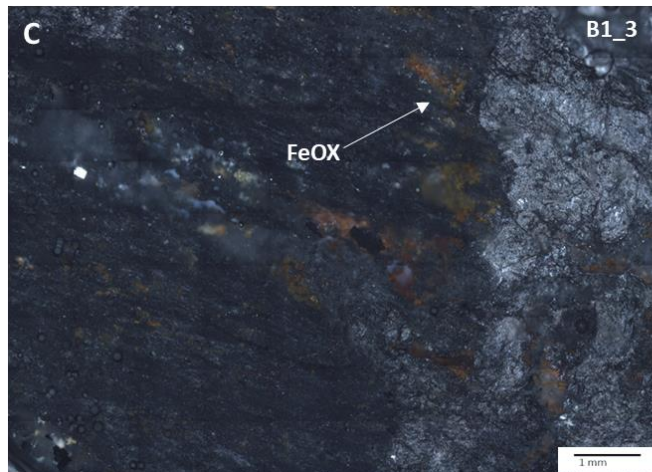
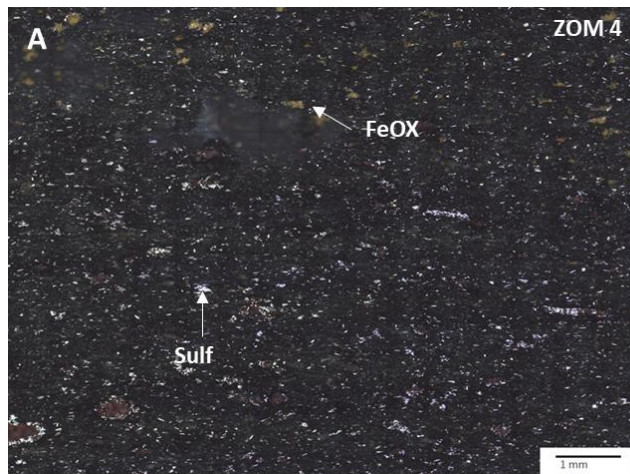
6.2. B – Petrographic general view of more siliceous character (polished blocks of rock pieces).

6.2. C – Petrographic general view of occurrence of iron oxides (FeOX; polished blocks of rock pieces).

6.2. D – General view of occurrence of iron oxides (FeOX; polished blocks of crushed sample).

6.2. E – General view of sample ZOM 10 (polished blocks of crushed sample).

6.2. F – General view of sample B4_3 with occurrence of some sulfides particles (Sulf; polished blocks of crushed sample).

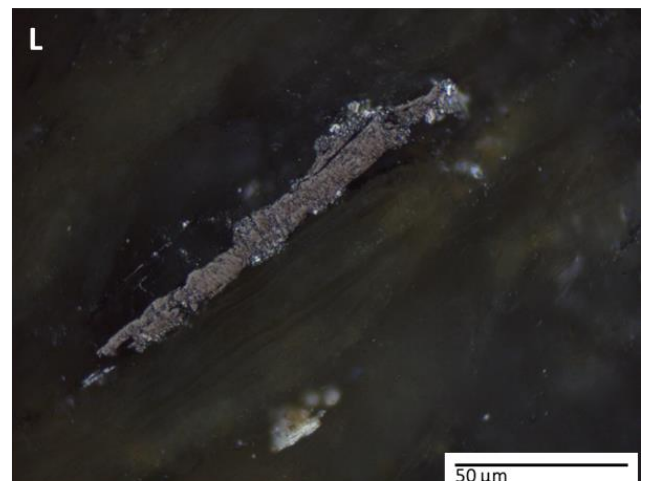
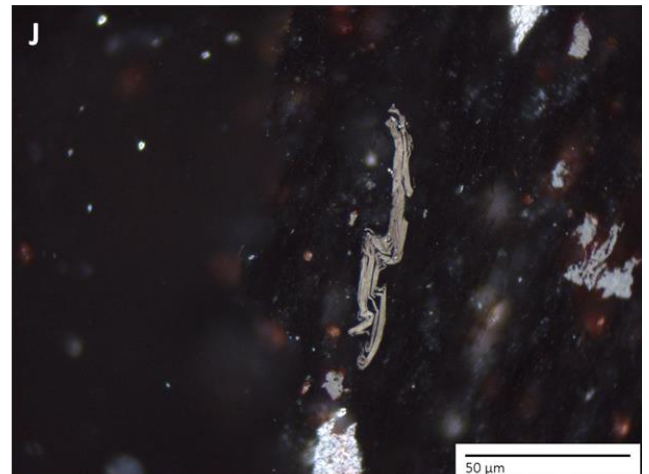
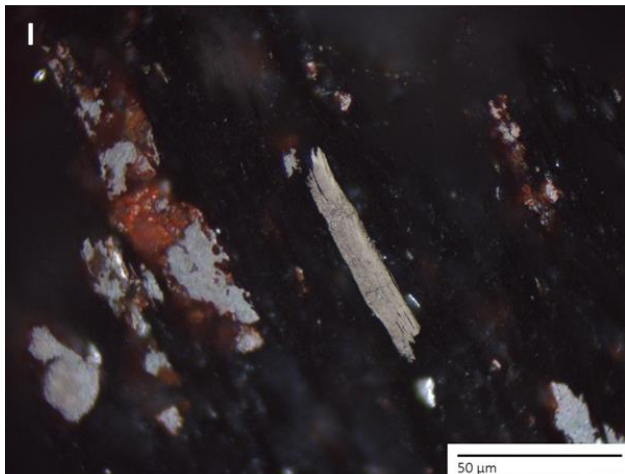
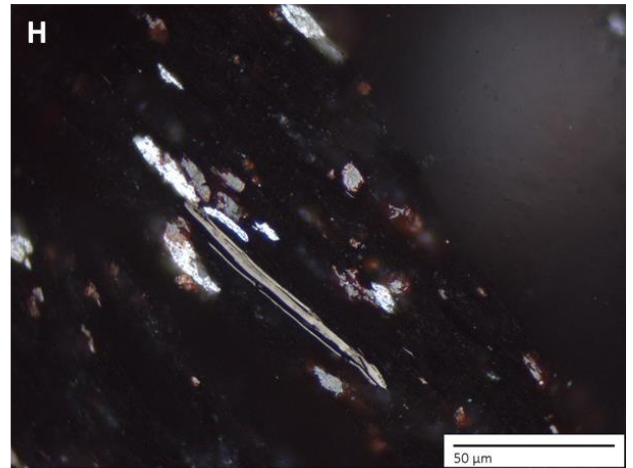
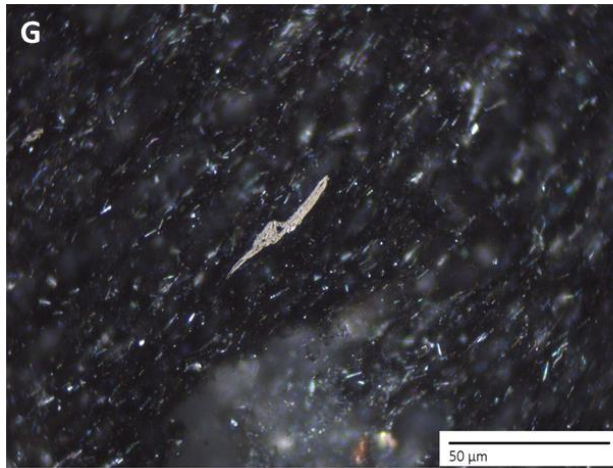


Petrographic aspects

6.2. G, H, I and J – Vitrinite-like particles exhibiting graphitic structure occurring as single flakes.

6.2. K – Vitrinite-like particles exhibiting graphitic structure occurring interbedded with sulfides and iron oxides.

6.2. L – Elongated vitrinite-like particle exhibiting graphitic structure occurring interbedded with iron oxides.



Petrographic aspects

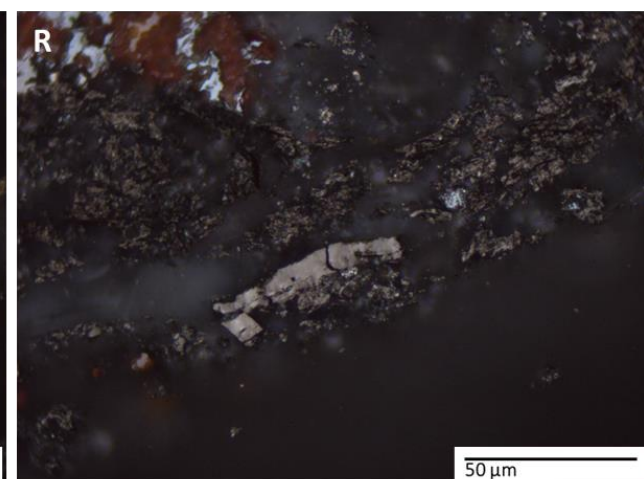
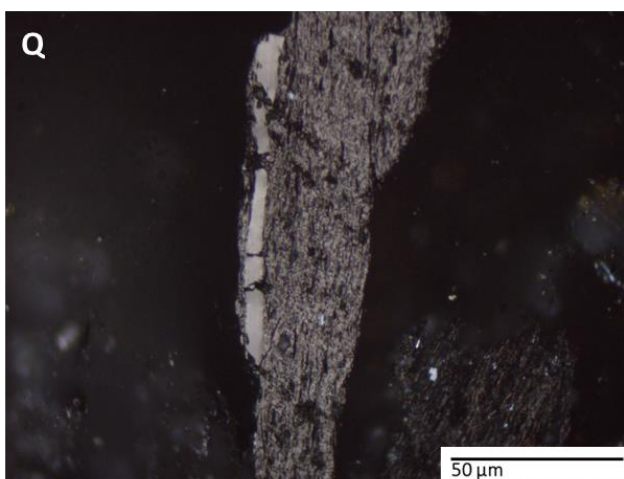
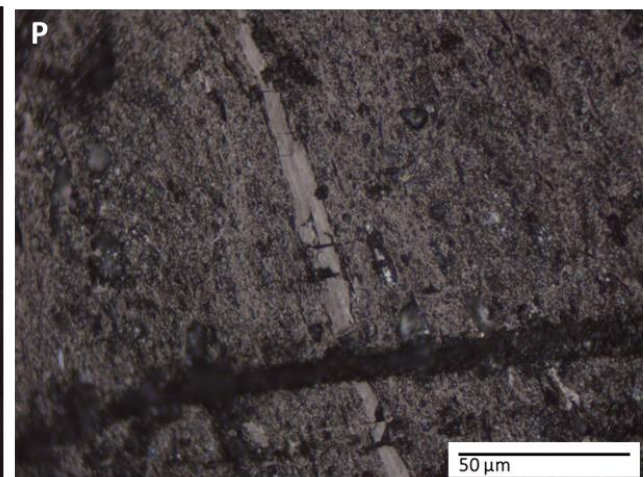
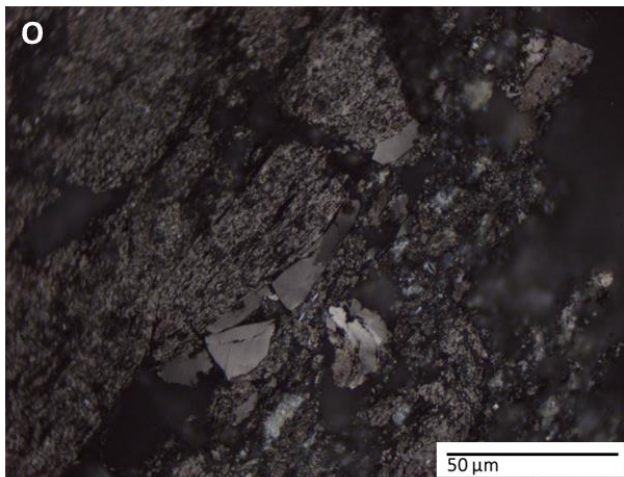
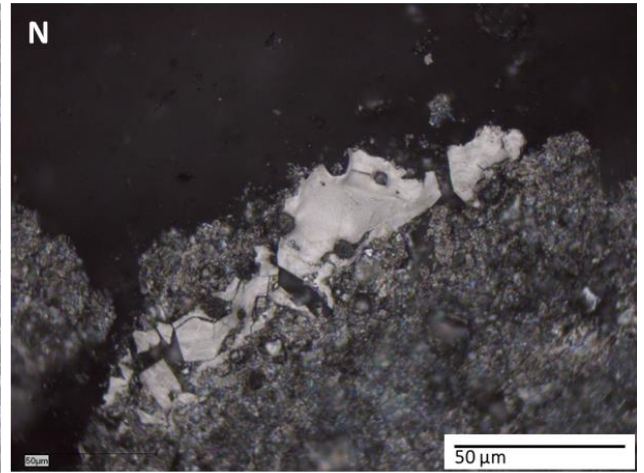
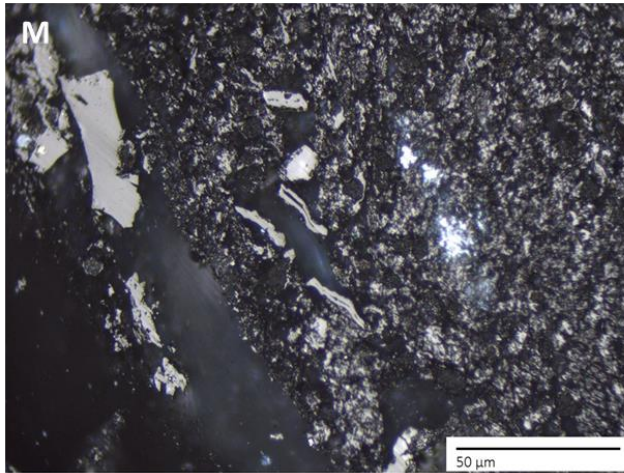
6.2. M – Graptolite fragments interbedded with vitrinite-like particles and some iron oxides particles.

6.2. N – Graptolite fragments displaying a fusellar layer and interbedded with vitrinite-like particles.

6.2. O – Graptolite fragments showing a segmented character occurring along vitrinite-like particles.

6.2. P and Q – Graptolite fragments showing an elongated rectangular shape and segmented character occurring along vitrinite-like particles.

6.2. R – Graptolite fragments occurring along vitrinite-like particles.

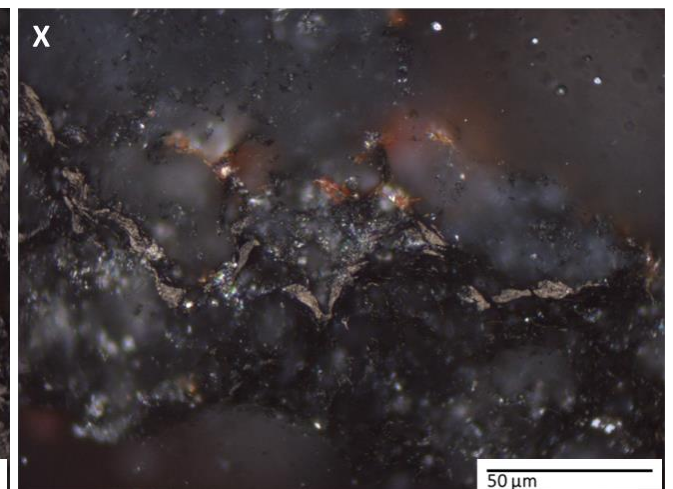
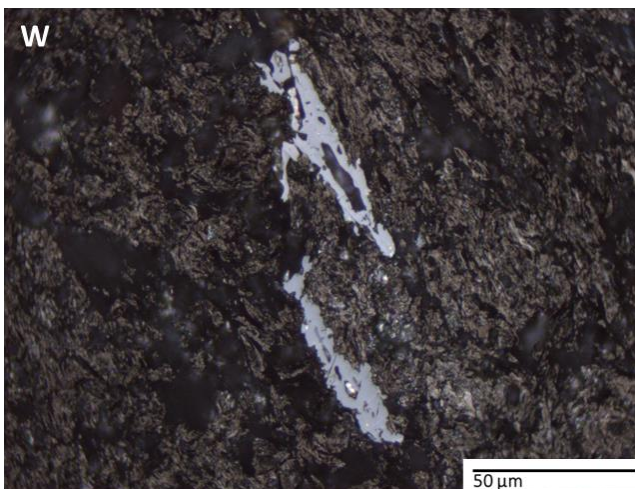
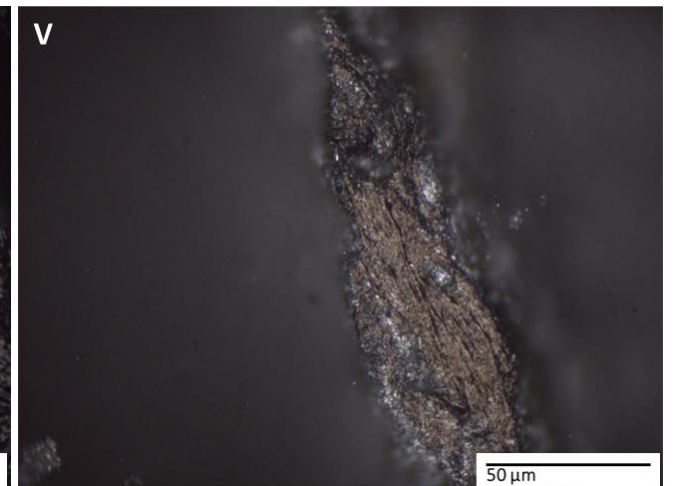
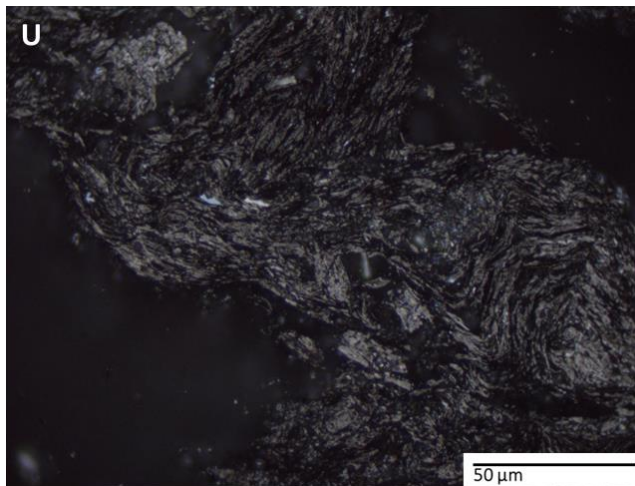
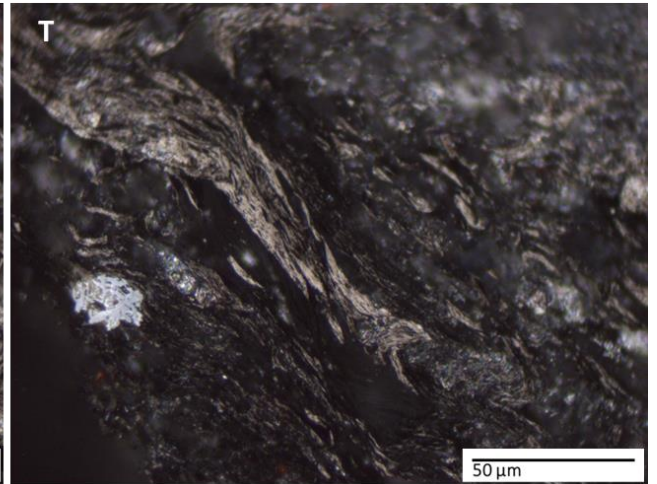
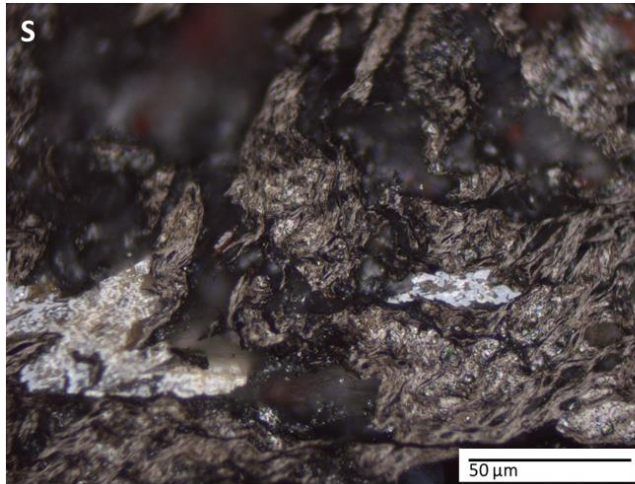


Petrographic aspects

6.2. S, T, U and V – Vitrinite-like particles thin and small in size, with varied morphology, occurring interbedded along mineral matter.

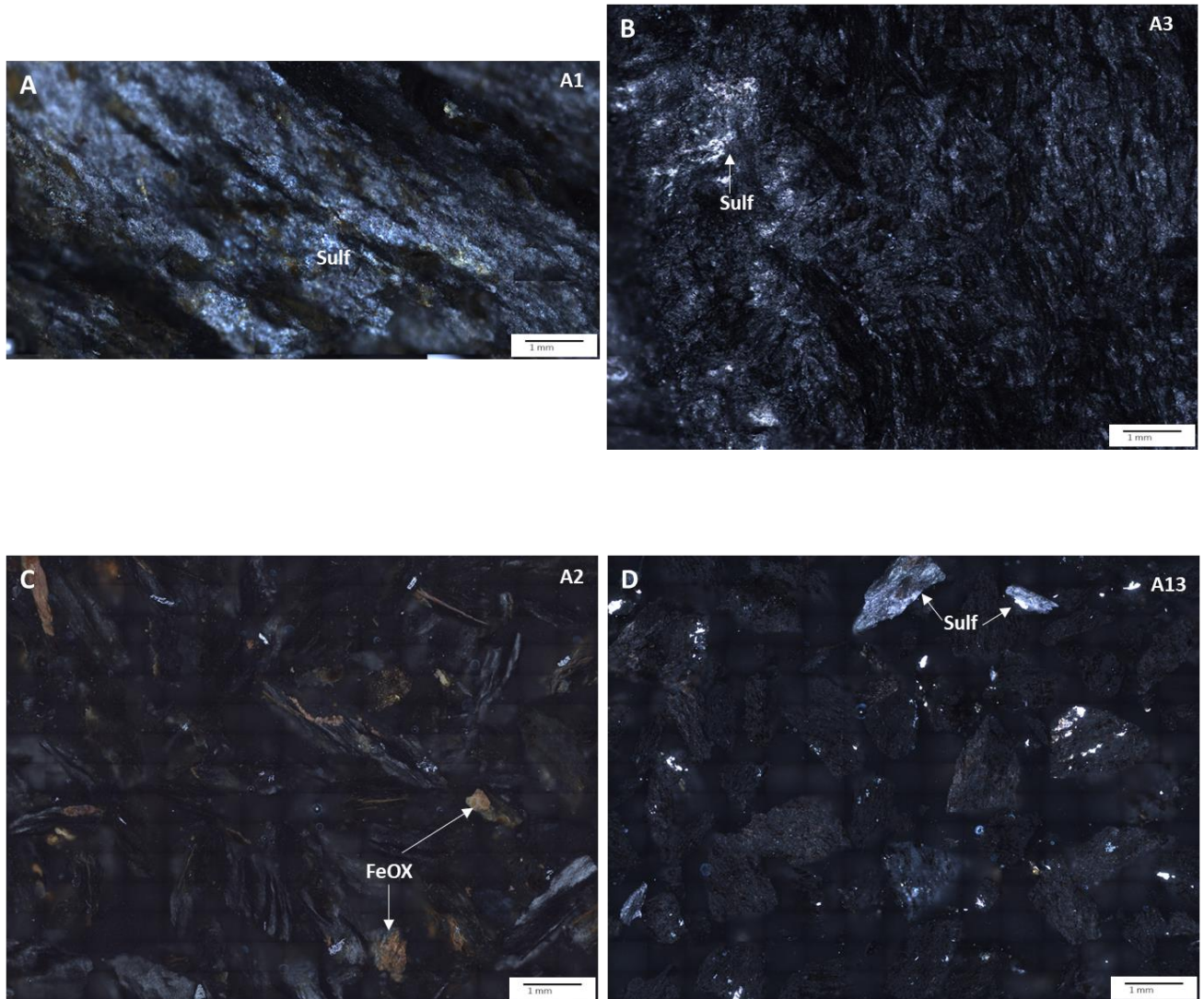
6.2. W – Vitrinite-like particles occurring along iron oxides.

6.2. X – Larger organic particles disseminated in fragments of interbedded mineral matter.



6.3. Cambrian black shales from Central Iberian Zone

Mosaics

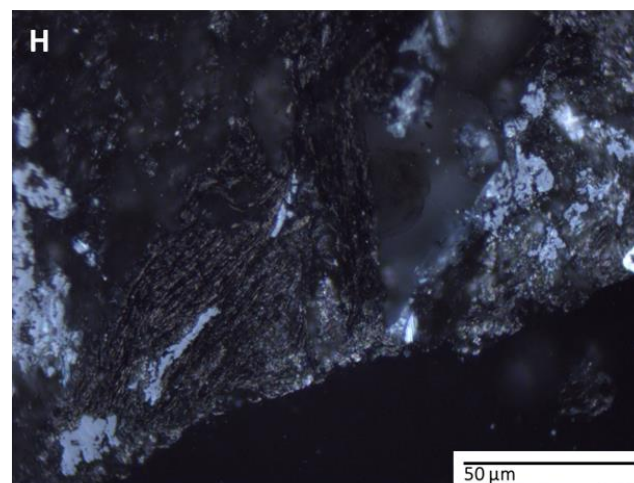
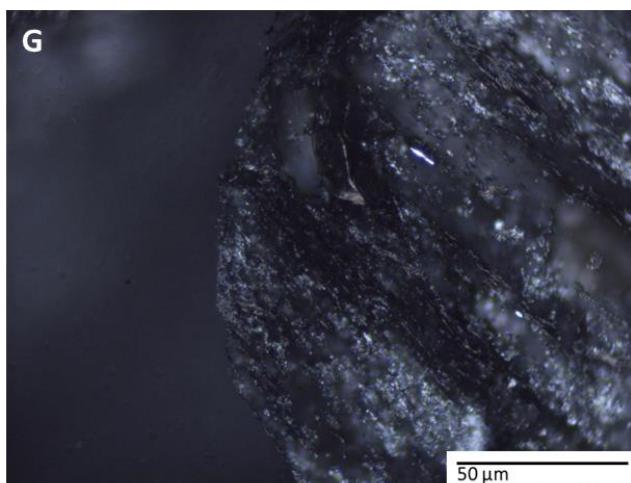
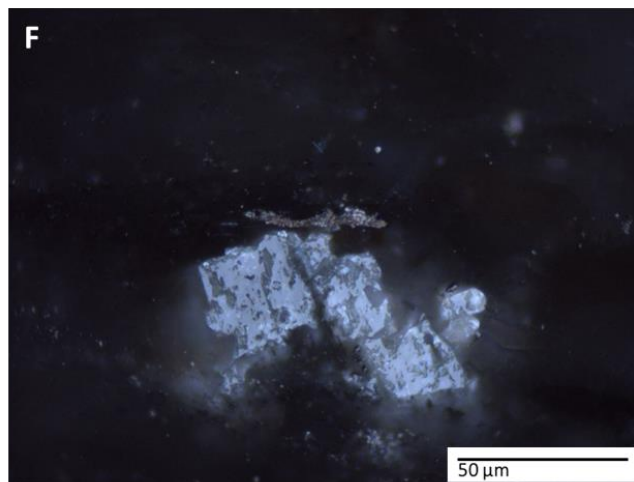
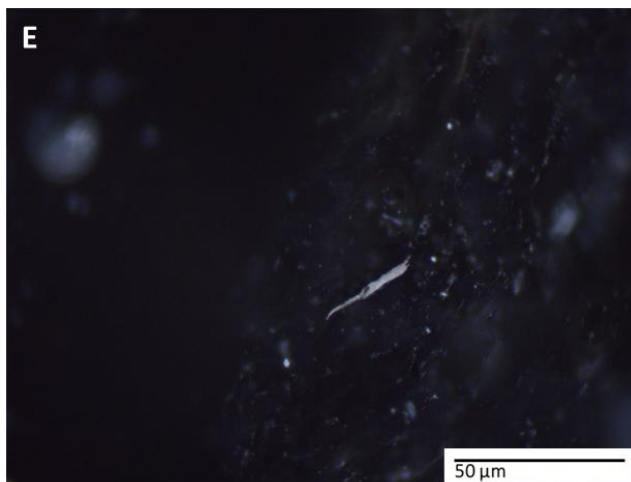


6.3. A and B – Petrographic general view of occurrence of sulfides (Sulf; polished blocks of rock pieces).

6.3. C – Petrographic general view of occurrence of iron oxides (FeOX; polished blocks of crushed sample).

6.3. D – Petrographic general view of occurrence of sulfides (Sulf; polished blocks of crushed sample).

Petrographic aspects



6.3. E and F – Vitrinite-like particles exhibiting graphitic structures and occurring as single flakes.

6.3. G and H – Vitrinite-like particles thin and small, occurring interbedded with mineral matter.

References

- Adams, J. A. S., Weaver, C. E., 1958. Thorium to uranium ratios as indicators of sedimentary processes-Examples of the concept of geochemical facies. *American Association of Petroleum Geologists Bulletin*, 42, 387-430.
- Ai, J. Y., George, S. C., Zhong, N. N., 2020. Organic geochemical characteristics of highly mature Late Neoproterozoic black shales from South China: Reappraisal of syngeneity and indigeneity of hydrocarbon biomarkers. *Precambrian Research* 336, 105508, 15 p. <https://doi.org/10.1016/j.precamres.2019.105508>.
- Alderton, D. H. M., Selby, D., Kucha, H., Blundell, D. J., 2016. A multistage origin for Kupferschiefer mineralization. *Ore Geology Reviews* 79, 535-543, <https://doi.org/10.1016/j.oregeorev.2016.05.007>.
- Algeo, T. J., Lyons, T. W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* 21, 1016 p. <https://doi.org/10.1029/2004PA001112>.
- Algeo, T. J., Maynard, J. B., 2004. Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chemical Geology*, 206, 289-318. <https://doi.org/10.1016/j.chemgeo.2003.12.009>.
- Alía, M., 1963. Rasgos estructurales de la Baja Extremadura. *Boletín Real Sociedad Española Historia Natural (Geología)*, 20, 247-262.
- Almeida, E., Pous, J., Monteiro Santos F., Fonseca, P., Marcuello, A., Queralt, P., Nolasco, R., Mendes-Victor, L., 2001. Electromagnetic imaging of a compressional tectonic in SW Iberia, *Geophysical Research Letters* 28, 439-442. <https://doi.org/10.1029/2000GL012037>.
- Anderson, G. M., Macqueen, R. W., 1982. Ore deposit models, 6. Mississippi-Valley-type lead-zinc deposits. *Geoscience Canada* 9, 108-117.
- Apalategui, O., Eguíluz, L., Quesada, C., 1990. Ossa-Morena zone: structure. *In*: Dallmeyer, R. D., Martínez-García, E. (Eds). *Pre-Mesozoic Geology of Iberia*, Springer-Verlag, 280-292.
- Araújo, A., Piçarra de Almeida, J., Borrego, J., Pedro, J., Oliveira, J. T., 2013. As Regiões Central e sul da Zona de Ossa Morena. *In*: Dias, R., Araújo, A., Terrinha, P., Kullberg,

J.C. (Eds). *Geologia de Portugal, Volume I, Geologia Pré-mesozóica de Portugal*, Escolar Editora, 509-549.

Arning, E. T., Lückge, A., Breuer, C., Gussone, N., Birgel, D., Peckmann, J., 2009. Genesis of phosphorite crusts off Peru. *Marine Geology*, 262, 68-81. <https://doi.org/10.1016/j.margeo.2009.03.006>.

ASTM D 7708-14, 2014. Standard Test Method for Microscopical Determination of the Reflectance of Vitrinite Dispersed in Sedimentary Rocks. ASTM International, 10 pp.

Baioumy, H., Ulfa, Y., Nawawi, M., Padmanabhan, E., Anuar, M., 2016. Mineralogy and geochemistry of Palaeozoic black shales from Peninsular Malaysia: Implications for their origin and maturation. *International Journal of Coal Geology* 165, 90-105.

Barker, C. E., 1991. Implications for organic maturation studies of evidence for a geologically rapid increase and stabilization of vitrinite reflectance at peak temperature: Cerro Pieto geothermal system. *Association of Petrology Geological Bulletin* 75, 1852-1863.

Barker, C. E., Pawlewicz, M. J., 1994. Calculation of vitrinite reflectance from thermal histories and peak temperatures - a comparison of methods. *In: Mukhopadhyay, P.K., Dow, W. G. (Eds.), Vitrinite reflectance as a Maturity Parameter. Applications and Limitations. In: Symposium Series 570. American Chemical Society*, 216-229. <https://doi.org/10.1021/bk-1994-0570.ch014>.

Bau, M., Dulski, P., 1996. Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa. *Precambrian Research*, Volume 79, Issues 1-2, 37-55. [https://doi.org/10.1016/0301-9268\(95\)00087-9](https://doi.org/10.1016/0301-9268(95)00087-9).

Bertrand, R., 1990. Correlations among the reflectances of vitrinite, chitinozoans, graptolites and scolecodonts. *Organic Geochemistry* 15, 565-574.

Betrant, B. S., Eric, B. E., Nkwankam, F. N., Nkongho, A. E., Maelle, N. T. F., Alex, Y. J., Cedric, B. B., Florent, A. D., Valentino, N. N., Emile, E., 2023. Organic vs inorganic contribution to the chemistry of cretaceous black shales in the Mamfe basin, SW Cameroon. Evidence from geochemistry and statistical analysis. *Heliyon* 9, Issue 3, e13748. <https://doi.org/10.1016/j.heliyon.2023.e13748>.

- Bhatia, M. R., Crook, K. A., 1986. Trace element characteristics of graywackes and tectonic setting discrimination of sedimentary basins. *Contributions to Mineralogy and Petrology*, 92(2), 181-193. <https://doi.org/10.1007/BF00375292>.
- Bokanda, E. E., Ekomane, E., Njilah, I. K., Fralick, P., Bisse, S. B., Tata, C. N., 2019. Inorganic geochemistry and petroleum source evaluation of organic black shale in the Mamfe Basin (West Africa). *Journal of Solid Earth* 4, 166-177. <https://doi.org/10.1016/j.sesci.2019.11.005>.
- Bonewitz, R., 2012. *Rocks and minerals*. 2nd ed. London: DK Publishing.
- Borg, G., Piestrzyński, A., Bachmann, G. H., Püttmann, W., Walther, S., Fiedler, M., 2012. An Overview of the European Kupferschiefer Deposits. *Society of Economic Geologists* 16, 455-486.
- Boyong, Y., Bin, H., Zhengyu, B., Zhaogan, Z., 2011. REE geochemical characteristics and depositional environment of the black shale-hosted Baiguoyuan Ag-V deposit in Xingshan, Hubei Province, China. *Journal of Rare Earths* 29, 5, 499-506.
- Canales, A., Matas, J., 1992. Anomalías de Au en el flanco Sur del Anticlinorio de Olivenza-Monesterio. In: Rábano, I., Gutierrez Marco, J. C. (Eds). *Libro de Resúmenes. VIII Reunión de Ossa Morena*, 53 pp.
- Carvalhosa, A., 1965. Contribuição para o conhecimento geológico da região entre Portel e Ficalho (Alentejo). *Memórias dos Serviços Geológicos de Portugal*, 11, 1-130.
- Chávez, W., 2000. Supergene oxidation of copper deposits: zoning and distribution of copper oxide minerals. *Society of Economic Geologists Newsletter* 41 (1), 10-21.
- Chichorro, M., Pereira, M. F., Díaz-Azpiroz, M., Williams, I. S., Fernandez, C., Pin, C., Silva, J. B., 2008. Cambrian ensialic rift-related magmatism in the Ossa-Morena Zone (Évora-Aracena metamorphic belt, SW Iberian Massif): Sm-Nd isotopes and SHRIMP zircon U-Th-Pb geochronology. *Tectonophysics* 461, 91-113. <https://doi.org/10.1016/j.tecto.2008.01.008>.
- Cisternas, M. E., Hermosilla, J., 2006. The role of bitumen in strata-bound copper deposit formation in the Copiapo area, Northern Chile. *Miner Deposita* 41, 339-355. <https://doi.org/10.1007/s00126-006-0063-9>.
- Coelho, J., 1990. Os “Skarns” cálcicos, pós-magmáticos, mineralizados em scheelite do Distrito Mineiro de Covas, Vila Nova de Cerveira, (Norte de Portugal). PhD Thesis, Faculty of Sciences of University of Porto, 570 p.

Condie, K. C., 1993. Chemical composition and evolution of the upper continental crust: contrasting results from surface samples and shales. *Chemical Geology* 104, 1-37. [https://doi.org/10.1016/0009-2541\(93\)90140-E](https://doi.org/10.1016/0009-2541(93)90140-E).

Cooper, R. A., Rigby, S., Loydell, D. K., Bats, D. E. B., 2012. Palaeoecology of the graptoloidea. *Earth Science Review* 112, 23-41. <https://doi.org/10.1016/j.earscirev.2012.01.001>.

Corrula, L. M., Branco, J. M. C., 2005. Área do Alandroal: Relatório do primeiro semestre de 2005 (Rio Narcea Gold Mines, S.A. - Sucursal em Portugal). International Report, LNEG, Lisbon (Not published).

Cortial, F., Gauthier-Lafaye, F., Lacrampe-Couloume, G., OBerlin, A., Weber, F., 1990. Characterization of organic matter associated with uranium deposits in the Francevillian Formation of Gabon (Lower Proterozoic). *Organic Geochemistry* 15, No. 1, 73-85. [https://doi.org/10.1016/0146-6380\(90\)90185-3](https://doi.org/10.1016/0146-6380(90)90185-3).

Coveney, R. M., 2000. Metalliferous shales and the role of organic matter with examples from China, Poland and the United States. In: Giordano, T. H., Kettler, R. M., Wood, S.A. (Eds.), *Ore Genesis and Exploration: The Roles of Organic Matter*. *Reviews in Economic Geology* 9, 251-280.

Coveney, R. M., Pašava, J., 2004. Special issue on black shales and related mineral deposits. *Ore Geology Reviews* 1-2, 167 pp.

Dai, S., Graham, I.T., Ward, C.R., 2016. A review of anomalous rare earth elements and yttrium in coal. *International Journal of Coal Geology* 159, 82-95. <https://doi.org/10.1016/j.coal.2016.04.005>.

Dai, S., Li, T., Jiang, Y., Ward, C.R., Hower, J.C., Sun, J., Liu, J., Song, H., Wei, J., Li, Q., Xie, P., 2015. Mineralogical and geochemical compositions of the Pennsylvanian coal in the Hailiushu Mine, Daqingshan Coalfield, Inner Mongolia, China: implications of sediment-source region and acid hydrothermal solutions. *International Journal of Coal Geology* 137, 92-110. <https://doi.org/10.3390/min8030104>.

Dawson, K. M., 1996. Skarn tungsten. In: Eckstrand, O. R., Sinclair, W. D., Thorpe, R. I. *Geology of Canadian Mineral Deposit Types* (Eds.). Geological Survey of Canada, *Geology of Canada* 8, 495-502.

DGEG - Direção Geral de Energia e Geologia. Available online: <https://www.dgeg.gov.pt/> (accessed on 18 January 2023).

- Dias, G., Leterrier, J., Mendes, A., Simões, P. P., Bertrand, J. M., 1998. U–Pb zircon and monazite geochronology of post-collisional Hercynian granitoids from the Central Iberian Zone (Northern Portugal). *Lithos* 45, 349-369.
- Dias, R., Araújo, A., Terrinha, P., Kullberg, J. C., 2013a. *Geologia de Portugal, Volume I: Geologia Pré-mesozóica de Portugal*, Escolar Editora, 807 pp.
- Dias, R., Araújo, A., Terrinha, P., Kullberg, J. C., 2013b. *Geologia de Portugal. Volume II: Geologia Meso-cenozóica de Portugal*, Escolar Editora, 798 pp.
- Dias, R., Coke, C., Ribeiro, A., 2022. Strain partitioning in the Variscan deformation of the Marão domain (Central Iberian zone; northern Portugal), *Journal of Structural Geology* 161, 104635, <https://doi.org/10.1016/j.jsg.2022.104635>.
- Dias, R., Ribeiro, A., Coke, C., Pereira, E., Rodrigues, J., Castro, P., Moreira, N., Rebelo, J., 2013c. Evolução estrutural dos setores setentrionais do Autóctone da Zona Centro-Ibérica. *In*: Dias, R., Araújo, A., Terina, P., Carlos Kullberg, J. *Geologia de Portugal, volume I, Geologia Pré-mesozóica de Portugal*. Escolar Editora, Lisboa, 95-97.
- Dias, R., Ribeiro, A., Romão, J., Coke, C., Moreira, N., 2016. A review of the Arcuate Structures in the Iberian Variscides; Constraints and Genetic Models. *Tectonophysics*, 681C, 170-194. <https://doi.org/10.1016/j.tecto.2016.04.011>.
- Dill, H., 1986. Metallogenesis of early Paleozoic graptolite shales from the Graefenthal Horst (Northern Bavaria - Federal Republic of Germany). *Economic Geology* 81, 889-903. <https://doi.org/10.2113/gsecongeo.81.4.889>.
- Disnar, J. R., Sureau, J. F., 1990. Organic matter in ore genesis: Progress and perspectives. *Organic Geochemistry* 16, 1-3, 577-599. [https://doi.org/10.1016/0146-6380\(90\)90072-8](https://doi.org/10.1016/0146-6380(90)90072-8).
- Distler, V. V., Yudovskaya, M. A., Mitrofanov, G. L., Prokof'ev, V.Yu., Lishnevskii, E. N., 2003. The Sukhoi Log noble metals deposit: geology, composition and genesis of mineralization. *Ore Geology Reviews* 24, 7-44.
- Distler, V. V., Yudovskaya, M. A., Mitrofanov, G. L., Prokof'ev, V. Y., Lishnevskii, E. N., 2004. Geology, composition, and genesis of the Sukhoi Log noble metals deposit, Russia, *Ore Geology Reviews* 24, Issues 1-2, 7-44. <https://doi.org/10.1016/j.oregeorev.2003.08.007>.
- Dozy, J. J., 1970. A geological model for the genesis of the lead–zinc ores of the Mississippi Valley, U.S.A. *Institute of Mining and Metallurgy Transactions* 79, 163-170.

- Dypvik, H., 1984. Geochemical compositions and depositional conditions of Upper Jurassic and Lower Cretaceous Yorkshire clays, England. *Geological Magazine* 121, 489-504. <https://doi.org/10.1017/S0016756800030028>.
- Eakin, P. A., Gize, A. P., 1992. Reflected-light microscopy of uraniferous bitumens. *Mineralogical Magazine* 56, 85-99. <https://doi.org/10.1180/minmag.1992.056.382.11>.
- Eguíluz, L., Gil Ibarguchi, J. I., Abalos, B., Apraiz, A., 2000. Superposed Hercynian and Cadomian orogenic cycles in the Ossa-Morena zone and related areas of the Iberian Massif. *Geological Society of America Bulletin* 112, 1398-1413. [https://doi.org/10.1130/0016-7606\(2000\)112<1398:SHACOC>2.0.CO;2](https://doi.org/10.1130/0016-7606(2000)112<1398:SHACOC>2.0.CO;2).
- Einaudi, M. T., Meinert, L. D., and Newberry, R. J., 1981. Skarn deposits: Economic Geology 75th Anniversary Volume, 317-391.
- El-Anwar, E. A. A., Mekky, H. S., Wahab, W. A., 2018. Geochemistry, mineralogy and depositional environment of black shales of the Duwi Formation, Qusseir area, Red Sea coast, Egypt. *Carbonates and Evaporites*, Springer 34, 883-892. <https://doi.org/10.1007/s13146-017-0417-7>.
- Elderfield, H., Greaves, M. J., 1982. The rare earth elements in seawater. *Nature* 296, 214-219. <https://doi.org/10.1038/296214a0>.
- Emerson, S. R., Husted, S. S., 1991. Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Marine Chemistry* 34, 177-196. [https://doi.org/10.1016/0304-4203\(91\)90002-E](https://doi.org/10.1016/0304-4203(91)90002-E).
- Eric, B. E., Philip, F., Emile, E., Isaac Konfor, N., Salomon Betrant, B., Daniel Florent, A., Bessa Armel Zacharie, E., 2019. Geochemical characteristics of shales in the Mamfe Basin, South West Cameroon: implication for depositional environments and oxidation conditions. *Journal of African Earth Sciences* 149, 131-142. <https://doi.org/10.1016/j.jafrearsci.2018.08.004>.
- Fang, X., Wu, L., Geng, A., Deng, Q., 2019. Formation and evolution of the Ediacaran to Lower Cambrian black shales in the Yangtze Platform, South China. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 527, 87-102. <https://doi.org/10.1016/j.palaeo.2019.04.025>.
- Farias, P., Gallastegui, G., González-Lodeiro, F., Marquínez, J., Martín Parra, L.M., Martínez Catalán, J.R., Pablo Maciá, J.G. de y Rodríguez Fernández, L.R., 1987.

Aportaciones al conocimiento de la litoestratigrafía y estructura de Galicia Central. Memórias da Faculdade de Ciências, Universidade do Porto, 411-431.

Fernandes, G., 2012. Mineralizações de Cobre da Mina de Miguel Vacas: Caracterização Petrográfica e Geoquímica. Master's thesis. Faculty of Sciences of the University of Lisbon, 345 pp.

Fernández-Suárez, J., Gutiérrez-Alonso, G., Jeffries, T. E., 2002. The importance of along margin terrane transport in northern Gondwana: insights from detrital zircon parentage in Neoproterozoic rocks from Iberia and Brittany. *Earth and Planetary Science Letters* 204, 75-88. [https://doi.org/10.1016/S0012-821X\(02\)00963-9](https://doi.org/10.1016/S0012-821X(02)00963-9).

Ferreira, E., Mateus, A., Azevedo, A. C., Duarte, L. V., Mendonça-Filho, J.G., Tassinari, C. C. G., 2020. Tracing bottom-water redox conditions during deposition of Lower and Upper Jurassic organic-rich sedimentary rocks in the Lusitanian Basin (Portugal): Insights from inorganic geochemistry. *Marine and Petroleum Geology* 117, 25 pp. <https://doi.org/10.1016/j.marpetgeo.2020.104343>.

Finkelman, R. B., 1981b. Modes of occurrence of trace elements in coal. *In*: USGS Open-File Report 81-99.

Finkelman, R. B., Palmer, C. A., Wang, P., 2018. Quantification of the modes of occurrence of 42 elements in coal. *International Journal of Coal Geology* 185, 138-160. <https://doi.org/10.1016/j.coal.2017.09.005>.

Finkelman, R.B., 1981a. The origin, occurrence, and distribution of the inorganic constituents in low-rank coals. *In*: Schobert, H. H., compiler, *Proceedings of the Basic Coal Science Workshop*. Grand Forks Energy Tech, 70-90.

Floyd, P. A., Leveridge, B. E., 1987. Tectonic environment of the Devonian Gramscatho basin, south Cornwall: framework mode and geochemical evidence from turbiditic sandstones. *Journal of the Geological Society of London* 144(4), 531-542. <https://doi.org/10.1144/gsjgs.144.4.0531>.

Foucaud, Y., Lechenard, B., Marion, P., Filippova, I., & Filippov, L., 2018. Geology, Textural Study, Ore Genesis and Processing of the Tabuaço Tungsten Deposit (Northern Portugal). *Contributions to Mineralization*. <http://dx.doi.org/10.5772/intechopen.71674>.

Galarraga, F., Reategui, K., Martínez, A., Martínez, M., Llamas, J.F., Marquez, G., 2008. V/Ni ratio as a parameter in palaeoenvironmental characterisation of nonmature

medium-crude oils from several Latin American basins. *Journal of Petroleum Science and Engineering* 61, 9-14. <https://doi.org/10.1016/j.petrol.2007.10.001>.

Gammon, J. B., 1966. Fahlbands in the Proterozoic of southern Norway. *Economic Geology* 61, 174-188.

Gao, P., Liu, G., Jia, C., Young, A., Wang, Z., Wang, T., Zhang, P., Wang, D., 2016. Redox variations and organic matter accumulation on the Yangtze carbonate platform during Late Ediacaran–Early Cambrian: Constraints from petrology and geochemistry. *Palaeogeography, Palaeoclimatology, Palaeoecology* 450, 91-110. <https://doi.org/10.1016/j.palaeo.2016.02.058>.

Gize, A. P., 1993. The analysis of organic matter in ore deposits. *In*: Parnell, J., Kucha, H., Landais, P. (Eds). *Bitumens in Ore Deposits: Special Publication on the Society for Geology Applied to Mineral Deposits*. Springer-Verlag, 28-52. https://doi.org/10.1007/978-3-642-85806-2_3.

Glikson, M., Mastalerz, M., 2000. *Organic Matter and Mineralisation: Thermal Alteration, Hydrocarbon Generation and Role in Metallogenesis*. Springer Dordrecht, 454 pp. <https://doi.org/10.1007/978-94-015-9474-5>.

Goinhas, J., 1985. A Prospeção Mineira em Portugal - Áreas Potenciais de Aplicação dos Projectos. General Directorate of Geology and Mines. *Bulletin and Mines*, 1.

Golder Associates Pty Ltd, 2020. *W Resources - Regua Tungsten Project, Portugal - Mineral Resource Statement*. Report, 26 pp.

Gomes, G. L., 2016. Spatial simulation of the W-Sn ore grades of São Pedro das Águias skarn mineral deposit (Tabuaço, northern Portugal). Dissertation for obtaining the master's degree in Geological Engineering, 126 pp.

Gonçalves, F., Carvalhosa, A., 1994. O Proterozóico da Zona de Ossa-Morena no Alentejo. *Síntese e Atualização de Conhecimentos*. *Memórias de Ciências*, 141-173.

Gonçalves, F., Oliveira, V., 1986. Alguns aspetos do Precâmbrico da Zona de Ossa Morena em Portugal. *O Proterozoico Superior de Estremoz*. *Memórias da Academia Ciências de Lisboa* 27, 111-117.

Gonçalves, P. A., Pinheiro, S., Mendonça Filho, J. G., Mendonça, J. O., Flores, D., 2020. Study of a Silurian sequence of Dornes region (Central Iberian Zone, Portugal): The contribution of organic petrology and palynofacies. *International Journal of Coal Geology* 225, 103501. <https://doi.org/10.1016/j.coal.2020.103501>.

Goodarzi, F., 1984. Organic petrography of graptolite fragments from Turkey. *Marine and Petroleum Geology* 1, 202-210. [https://doi.org/10.1016/0264-8172\(84\)90146-6](https://doi.org/10.1016/0264-8172(84)90146-6).

Goodarzi, F., 1985. Dispersion of optical properties of graptolite epiderms with increased maturity in early Paleozoic organic-rich sediments. *Fuel* 64, 1735-1740. [https://doi.org/10.1016/0016-2361\(85\)90401-6](https://doi.org/10.1016/0016-2361(85)90401-6).

Goodarzi, F., Gentzis, T., Harrison, C., Thorsteinsson, R., 1992. The significance of graptolite reflectance in regional thermal maturity studies, Queen Elizabeth Islands, Arctic Canada. *Organic Geochemistry* 18, 347-357. [https://doi.org/10.1016/0146-6380\(92\)90075-9](https://doi.org/10.1016/0146-6380(92)90075-9).

Goodarzi, F., Norford, B.S., 1987. Optical properties of graptolite epiderma review. *Bulletin Geological Society of Denmark* 35, 141-147.

Greenwood, P. F., Brocks, J. J., Grice, K., Schwark, L., Jaraula C. M. B., Dick, J. M., Evans, K. A., 2013. Organic geochemistry and mineralogy. I. Characterization of organic matter associated with metal deposits. *Ore Geology Reviews* 50, 1-27. <http://dx.doi.org/10.1016/j.oregeorev.2012.10.004>.

Gromet, L. P., Dymek, R. F., Haskin, L. A., Korotev, R. L., 1984. The "North American shale composite": Its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta* 48, 2469-2482. [https://doi.org/10.1016/0016-7037\(84\)90298-9](https://doi.org/10.1016/0016-7037(84)90298-9).

Guilbert, J. M., Park, C. F., 1986. *The Geology of Ore Deposits*. W.H. Freeman and Company, 985 pp.

Guo, S., Chen, Y., Chuan-Zhou Liu, Jian-Gang Wang, Su, B., Yi-Jie Gao, Fu-Yuan Wua, Sein, K., Yue-Heng Yang, Maoa, Q., 2016. Scheelite and coexisting F-rich zoned garnet, vesuvianite, fluorite, and apatite in calc-silicate rocks from the Mogok metamorphic belt, Myanmar: Implications for metasomatism in marble and the role of halogens in W mobilization and mineralization. *Journal of Asian Earth Sciences* 117, 82-106.

Gürdal, G., 2008. Geochemistry of trace elements in Çan coal (Miocene), Çanakkale, Turkey. *International Journal of Coal Geology* 74, 28-40. <https://doi.org/10.1016/j.coal.2007.09.004>.

Hackley, P. C., Guevara, E. H., Hentz, T. F., Hook, R. W., 2009. Thermal maturity and organic composition of Pennsylvanian coals and carbonaceous shales, north-central Texas: implications for coalbed gas potential. *International Journal of Coal Geology* 77, 294-309.

Haldar, S. K., 2020. Chapter 7 - Metamorphic rocks. Introduction to Mineralogy and Petrology (Second Edition), Elsevier, 269-289.

Hallberg, R. O., 1976. A geochemical method for investigation of palaeoredox conditions in sediments. *Ambio Special Report* 4, 139-147.

Hallberg, R. O., 1982. Diagenetic and environmental effects on heavy-metal distribution in sediments: A hypothesis with an illustration from the Baltic Sea. *In*: Fanning, K. A., Manheim, F. T. (Eds), *The Dynamic Environment of the Ocean Floor*, 305-316.

Hartkopf-Fröder, C., Königshof, P., Littke, R., Schwarzbauer, J., 2015. Optical thermal maturity parameters and organic geochemical alteration at low grade diagenesis to anchimetamorphism: A review. *International Journal of Coal Geology* 150-151, 74-119. <https://doi.org/10.1016/j.coal.2015.06.005>.

Hatch, J. R., Leventhal, J. S., 1992. Relationship between inferred redox potential of the depositional environment and geochemistry of the upper Pennsylvanian (Missourian) stark shale member of the Dennis Limestone, Wabaunsee County, Kansas, USA. *Chemical Geology* 99, 65-82. [https://doi.org/10.1016/0009-2541\(92\)90031-Y](https://doi.org/10.1016/0009-2541(92)90031-Y).

Hunt, J. M., 1996. *Petroleum Geochemistry and Geology* (2nd Eds). W. H. Freeman and Company, New York, 743 pp.

Huyck, H. L. O., 1989. When is a metalliferous black shale not a black shale? *In*: *Metalliferous Black Shales and Related Ore Deposits – Proceedings, United States Working Group Meeting, International Geological Correlation Program Project 254*. U. S. Geological Survey Circular 1058, 42-56.

ISO 7404-2, 2009. *Methods for the petrographic analysis of Coals - Part 2: Methods of preparing coal samples*, 12 pp.

Jones, B., Manning, D., 1994. Comparison of geochemical indices used for the interpretation of palaeoredox conditions in ancient mudstones. *Chemical Geology* 111, 111-129. [https://doi.org/10.1016/0009-2541\(94\)90085-X](https://doi.org/10.1016/0009-2541(94)90085-X).

Julivert, M., Fontboté, J.M., Ribeiro, A. y Conde, L., 1972. *Mapa Tectónico de la Península Ibérica y Baleares Escala 1:1 000 000*. Instituto Geológico y Minero de España, Madrid.

Kamber, B. S., Webb, G. E., 2001. The geochemistry of late Archaean microbial carbonate: Implications for ocean chemistry and continental erosion history. *Geochimica et Cosmochimica Acta* 65, 2509-2525. [https://doi.org/10.1016/S0016-7037\(01\)00613-5](https://doi.org/10.1016/S0016-7037(01)00613-5).

- Ketris, M. P., Yudovich, Y. E., 2009. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. *International Journal of Coal Geology* 78, 135-148. <https://doi.org/10.1016/j.coal.2009.01.002>.
- Kontinen, A., Hanski, E., 2015. The Talvivaara Black Shale-Hosted Ni-Zn-Cu-Co Deposit in Eastern Finland. *Mineral Deposits of Finland*, Elsevier, 557-612. <https://doi.org/10.1016/B978-0-12-410438-9.00022-4>.
- Kunzmann, M., Halverson, G. P., Scott, C., Minarik, W. G., Wing, B. A., 2015. Geochemistry of Neoproterozoic black shales from Svalbard: Implications for oceanic redox conditions spanning Cryogenian glaciations. *Chemical Geology* 417, 383-393. <https://doi.org/10.1016/j.chemgeo.2015.10.022>.
- Kwak, T. A. P., 1987. W-Sn skarn deposits and related metamorphic skarns and granitoids. *Developments in economic geology* 24, 439 pp.
- Kwak, T.A.P., 1986. Fluid inclusions in skarns (carbonate replacement deposits): *Journal of Metamorphic Geology* 4, 363-384.
- Kwiecinska, B., Petersen, H. I., 2004. Graphite, semi-graphite, natural coke, and natural char classification-ICCP system. *International Journal of Coal Geology* 57, 99-116. <https://doi.org/10.1016/j.coal.2003.09.003>.
- Lajoinie, M. F., Ballivián Justiniano, C. A., Salvioli, M. A., Ruiz, R., Recio, C., Sial, A. N., Etcheverry, R. O., Curci, M. V., de la Cal, H. F., Lanfranchini, M. E., 2019. Significance of graphite inclusion occurrence in the minerals of the San Miguel skarn for the Palaeoproterozoic basement of Tandilia Belt (Argentina) and for the Río de la Plata Craton. *Journal of South American Earth Sciences* 89, 118-139. <https://doi.org/10.1016/j.jsames.2018.11.008>.
- Landais, P., 1993. Bitumens in uranium deposits. *In*: Parnell, J., Kucha, H., Landais, P. (Eds), *Bitumens in Ore Deposits: Special Publication on the Society for Geology Applied to Mineral Deposits* 9, 213-235.
- Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., H., Flores, D., 2023a. Geochemistry of Precambrian black shales from Ossa-Morena Zone (Portugal): depositional environment and possible source of metals. *Journal of Iberian Geology*. <https://doi.org/10.1007/s41513-022-00202-6>.
- Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., Mendonça Filho, J.G., Flores, D., 2019. Caracterização geoquímica da matéria orgânica de xistos negros associados a

mineralização de Cu na Zona Ossa Morena. Extended abstracts XII Iberian Congress of Geochemistry, 187-190.

Laranjeira, V., Ribeiro, J., Moreira, N., Nogueira, P., Mendonça Filho, J.G., Flores, D., 2023b (in press). Petrographic and geochemical characterization of organic matter in Precambrian black shales from Ossa-Morena Zone, South of Portugal. *In*: Chaminé, H.I., Fernandes, J.A. (Eds.), *Advances in Geoengineering, Geotechnologies, and Geoenvironment for Earth Systems and Sustainable Georesources Management - Proceedings of the 1st Conference on Georesources, Geomaterials, Geotechnologies and Geoenvironment (4GEO)*, Springer ASTI Series.

Large, R. R., Bull, S. W., Maslennikov V. V., 2011. A Carbonaceous Sedimentary Source-Rock Model for Carlin-Type and Orogenic Gold Deposits. *Society of Economic Geologists, Economic Geology* 106, 331-358.

Lefebvre, M. G., Romer, R. L., Glodny, J., 2019. The Hämmerlein skarn-hosted polymetallic deposit and the Eibenstock granite associated greisen, western Erzgebirge, Germany: two phases of mineralization - two Sn sources. *Miner Deposita* 54, 193-216. <https://doi.org/10.1007/s00126-018-0830-4>.

Leventhal, J. S., 1986. Roles of organic matter in ore deposits. *In*: Dean, W. E. (Eds), *Organics and Ore Deposits*. Denver Regional Exploration Society, 7-20. https://doi.org/10.1007/978-1-4615-2890-6_25.

Leventhal, J., 1993. Metals and black shales. *In*: Engel, M. H., Macko, S. A. (Eds), *Organic Geochemistry - Principles and Applications*. Plenum Press, New York, 581-592. <https://doi.org/10.1007/978-1-4615-2890-6>.

Leybourne, M. I., Goodfellow, W. D., Boyle, D. R., Hall, G. M., 2000. Rapid development of negative Ce anomalies in surface waters and contrasting REE patterns in groundwaters associated with Zn–Pb massive sulphide deposits. *Applied Geochemistry* 15 (6), 695-723. [https://doi.org/10.1016/S0883-2927\(99\)00096-7](https://doi.org/10.1016/S0883-2927(99)00096-7).

Li, J., Qin, Y., Chen, Y., Shen, J., 2022. Microstructural Characteristics of Graphite Microcrystals in Graphitized Coal: Insights from Petrology, Mineralogy and Spectroscopy. *Minerals* 12, 1189. <https://doi.org/10.3390/min12101189>.

Lin, Y., Zheng, M., Ye, C., Power, I. A., 2019. Trace and rare earth element geochemistry of Holocene hydromagnesite from Dujiali Lake, central Qinghai-Tibetan Plateau, China. *Carbonates Evaporites* 34, 1265-1279. <https://doi.org/10.1007/s13146-017-0395-9>.

- Liñán, E., Quesada, C., 1990. Ossa-Morena Zone: Stratigraphy, rift phase (Cambrian). *In: Martinez, E., Dallmeyer, R. D., (Eds). Pre-Mesozoic Geology of Iberia, Springer Verlag, 259-266.*
- Linnemann, U., Pereira, M. F., Jeffries, T., Drost, K., Gerdes, A., 2008. Cadomian Orogeny and the opening of the Rheic Ocean: New insights in the diachrony of geotectonic processes constrained by LA-ICP-MS U-Pb zircon dating (Ossa-Morena and Saxo-Thuringian Zones, Iberian and Bohemian Massifs). *Tectonophysics* 361, 21-43. <https://doi.org/10.1016/j.tecto.2008.05.002>.
- Liu, J., Yang, Z., Yan, X., Ji, D., Yang, Y., Hu, L., 2015. Modes of occurrence of highly-elevated trace elements in superhigh-organic-sulfur coals. *Fuel* 156 (15), 190-197.
- LNEG - Laboratório Nacional de Energia e Geologia. Available online: <http://www.lneg.pt/> (accessed on 26 January 2023).
- LNEG, 2010. Geological map of Portugal at 1:1 000 000. 3rd edition. National Laboratory of Energy and Geology, Lisbon.
- Locutura, J., Tornos, F., Florido, P., Baeza, L., 1990. Ossa-Morena Zone: Metallogeny. *In: Martinez, E., Dallmeyer, R. D., (Eds), Pre-Mesozoic Geology of Iberia, Springer Verlag, 321-332.*
- Lopes, L., 2015. Litogeoquímica na área de concessão da Boa-Fé (Colt Resources). MSc Thesis (unpublished), Universidade de Aveiro, 132 pp.
- Lopes, L., Santos, J. F., Sousa, J. C., Ribeiro, S., 2015. Novos dados petrográficos, geoquímicos e isotópicos sobre a área de concessão de Boa Fé (Montemor-o-Novo, Zona de Ossa-Morena). *Comunicações Geológicas* 102, Volume Especial I, 153-156.
- López-Guijarro, R., 2006. Ambiente geodinámico y procedencia de las rocas sedimentarias precámbricas de las zonas de Ossa Morena y Centroibérica a través del análisis geoquímico. *Boletín Geológico Minero* 117, 499-505.
- López-Guijarro, R., Armendáriz, M., Quesada, C., Fernández-Suárez, J., Murphy, J. B., Pin, C., Bellido, F., 2008. Ediacaran-Palaeozoic tectonic evolution of the Ossa Morena and Central Iberian zones (SW Iberia) as revealed by Sm-Nd isotope systematics. *Tectonophysics* 461, 202-214. <https://doi.org/10.1016/j.tecto.2008.06.006>.
- Lotze, F., 1945. Zur Gliederung der Varisziden der Iberischen Meseta. *Geotektonische Forschungen* 6, 78-92.

Loukola-Ruskeeniemi, K., Lahtinen, H., 2013. Multiphase evolution in the black-shale-hosted Ni-Cu-Zn-Co deposit at Talvivaara, Finland. *Ore Geology Reviews* 52, 85-99. <https://doi.org/10.1016/j.oregeorev.2012.10.006>.

Luo, Q., Zhong, N., Dai, N., Zhang, W., 2016. Graptolite-derived organic matter in the Wufeng-Longmaxi Formations (Upper Ordovician–Lower Silurian) of southeastern Chongqing, China: Implications for gas shale evaluation. *International Journal of Coal Geology* 153, 87-98. <http://dx.doi.org/10.1016/j.coal.2015.11.014>.

Lyons, T. W., Werne, J. P., Hollander, D. J., Murray, R. W., 2003. Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela. *Chemical Geology* 195, 131-157. [https://doi.org/10.1016/S0009-2541\(02\)00392-3](https://doi.org/10.1016/S0009-2541(02)00392-3).

Maia, M., Moreira, N., Mirão, J., Noronha, F., Nogueira, P., 2019. Fluid inclusions study of Cu-rich deposits from Sousel-Barrancos metallogenic belt (Ossa-Morena Zone, Portugal). *Mineralogic and Petrographic Protocol Abstract Series (ECROFI 2019)* 10, 79.

Maia, M., Moreira, N., Vicente, S., Mirão, J., Noronha, F., Nogueira, P., 2020. Multi-Stage Fluid System Responsible for Ore Deposition in the Ossa-Morena Zone (Portugal): Constraints in Cu-Ore Deposits Formation. *Geology of Ore Deposits* 62 (6), 508-534. <https://doi.org/10.1134/S1075701520060094>.

Maia, M., Roseiro, J., Nogueira, P., Noronha, F., Fuertes-Fuente, M., Cepedal, A., Mirão, J., 2022. New insights on the Escoural Orogenic gold district (Ossa-Morena Zone, SW Iberia): Geochemistry, fluid inclusions and stable isotope constraints from the Monfurado gold prospect. *Ore Geology Reviews*, 142. <https://doi.org/10.1016/j.oregeorev.2022.104736>.

Martínez, F. J., Rolet, J., 1988. Late Palaeozoic metamorphism in the northwestern Iberian Peninsula, Brittany and related areas in SW Europe. Geological Society, London, Special Publications 38, 611-620.

Martínez-Catalán, J. R., Martínez Poyatos, D., Bea, F., 2004. Zona Centroibérica: Introducción. In: Vera, J.A. (Eds.), *Geología de España*. SGE-IGME, Madrid, 68-69.

Martins, L. P., 2012. Mineral Resources of Portugal. Direcção Geral de Energia e Geologia, Lisbon, 71 pp.

Mateus, A., Matos, J. X., Rosa, C., Oliveira, V., 2003. Cu-ores in quartz-carbonate veins at Estremoz-Alandroal and Barrancos-Sto Aleixo regions (Ossa-Morena Zone): a result

of Late-Variscan hydrothermal activity. VI National Congress of Geology, Lisbon (Portugal), F90-F93.

Mateus, A., Munhá, J., Inverno, C., Matos, J., Martins, L., Oliveira, D., Jesus, A., Salgueiro, R., 2013. Mineralizações no sector português da Zona de Ossa-Morena. Geologia de Portugal, Volume I - Geologia Pré-mesozóica de Portugal. *In*: Dias, R., Araújo, A., Terrinha, P., Kullberg, J. C. (Eds), Escolar Editora, 577-615.

Matos, J. X, Filipe, A., 2013. Carta de Ocorrências Mineiras do Alentejo e Algarve, Escala 1:400 000. National Laboratory of Energy and Geology.

Matos, J. X., Rosa, C., 2001. Diagnóstico Preliminar de Minas Abandonadas - Área Sul. Internal Report IGM, 276 pp.

Maynard, J. B., Elswick, E. R., Hower, J. C., 2001. Reflectance of dispersed vitrinite in shales hosting Pb–Zn–Cu ore deposits in western Cuba: comparison with clay crystallinity. *International Journal of Coal Geology* 47, 161-170. [https://doi.org/10.1016/S0166-5162\(01\)00040-4](https://doi.org/10.1016/S0166-5162(01)00040-4).

Meinert, L. D., 1992. Skarns and skarn deposits. *In*: Geoscience Canada 19, 145-162.

Meinert, L., Dipple, G., Nicolescu, S., 2005. World skarn deposits. *In*: Society of Economic Geologists, Economic Geology 100th Anniversary Volume, 299-336.

Melchin, M. J., Sadler, P. M., Cramer, B. D., 2012. The Silurian Period. *In*: Gradstein, F. M., Ogg, J. G., Schmitz, M., Ogg G. M. (Eds.), The Geologic Time Scale 2, 525-558.

Mendonça Filho, J.G., Gonçalves, P.A., 2017. Organic Matter: Concepts and Definitions, Chapter 1. *In*: Suárez-Ruiz, I., Mendonça Filho, J.G. (Eds.), Geology: Current and Future Developments. The Role of Organic Petrology in the Exploration of Conventional and Unconventional Hydrocarbon Systems. Bentham Science Publishers, United Arab Emirates 1, 1-33.

Meyers, P. A., Pratt, L. M., Nagy, B., 1992. Geochemistry of metalliferous black shales. *Chemical Geology* 99, 211 pp.

Moreira, N., Araújo, A., Pedro, J. C., Dias, R., 2014a. Evolução geodinâmica da Zona de Ossa-Morena no contexto do SW Ibérico durante o Ciclo Varisco. *Comunicações Geológicas* 101, Volume Especial I, 275-278.

- Moreira, N., Dias, R., Pedro, J. C., Araújo, A., 2014b. Interference between Variscan deformation events in Torre de Cabedal structure: Alter-do-Chão – Elvas sector (Ossa-Morena Zone). *Comunicações Geológicas* 101, Volume Especial I, 279-282.
- Moreira, N., Pedro, J., Santos, J. F., Araújo, A., Dias, R., Ribeiro, S., Romão, J., Mirão, J., 2019. $^{87}\text{Sr}/^{86}\text{Sr}$ applied to age discrimination of the Palaeozoic carbonates of the Ossa-Morena Zone (SW Iberia Variscides). *International Journal of Earth Sciences* 108(3), 963-987.
- Mossman, D. J., 1999. Carbonaceous substances in mineral deposits: implications for geochemical exploration. *Journal of Geochemical Exploration* 66, 241-247.
- Mossman, D. J., Minter, W. E. L., Dutkiewicz, A., Hallbauer, D. K., George, S. C., Hennigh, Q., Reimer, T. O., Horscroft, F. D., 2008. The indigenous origin of Witwatersrand “carbon”. *Precambrian Research* 164, 173-186.
<https://doi.org/10.1016/j.precamres.2008.04.008>.
- Munteanu, M., Marinacea, S., Kasper, H.U., Zak, K., Alexe, V., Mihalache, A., Cristea, C., Trandafir, V., Saptefrati, G., Mihalache, A., 2003. Black chert-hosted manganese deposits from the eastern Carpathians of Romania: petrography, genesis and metamorphic evolution. *Ore Geology Reviews* 24, 45-65.
<https://doi.org/10.1016/j.oregeorev.2003.08.004>.
- Murray, R. W., Buchholz ten Brink, M. R., Jones, D. L., Gerlach, D. C., Russ, G. P., 1990. Rare earth elements as indicators of different marine depositional environments in chert and shale. *Geology* 18, 268-271.
- Noronha, F., Ribeiro, M.A., Almeida, A., Dória, A., Guedes, A., Lima, A., Martins, H.C.B., Sant'Ovaia, H., Nogueira, P., Martins, T., Ramos, R., Romeu, R., 2013. Jazigos Filonianos Hidrotermais e Aplitopegmatíticos Especialmente Associados a Granitos (Norte de Portugal). *In*: Dias, R., Araújo, A., Terrinha, P., Kulberg, J. C., (Eds), *Geologia em Portugal. Geologia Pré-Mesozoica de Portugal*. Escolar Editora 1, 403-438.
- Oliveira, D. P. S., Reed, R. M., Milliken, K. L., Robb, L. J., Inverno, C. M. C., D'Orey, F. L. C., 2003. Série Negra black quartzites - Tomar Cordoba Shear Zone, E Portugal: mineralogy and cathodoluminescence studies. *Cuadernos Laboratorio Xeológico de Laxe* 28, 193-211.
- Oliveira, D. P. S., Robb, L. J., Inverno, C. M. C., Charlesworth, E. G., 2007. Metallogenesis of the São Martinho and Mosteiros Gold Deposits, Tomar Cordoba Shear

Zone, Portugal. *International Geology Review* 49, 10, 907-930.
<https://doi.org/10.2747/0020-6814.49.10.907>.

Oliveira, J. T., Oliveira, V., Piçarra, J. M., 1991. Traços gerais da evolução tectono-estratigráfica da Zona de Ossa Morena em Portugal. *Cuadernos Laboratorio Xeolóxico de Laxe* 16, 221-250.

Oliveira, J. T., Pereira, E., Ramalho, M. M., Antunes, M. T., Monteiro, J. H., 1992. Carta Geológica de Portugal à escala 1:500 000 - Folha Norte e Folha Sul. Serviço Geológico Português, Lisboa.

Oliveira, J. T., Rosa, C. J. P., Pereira Z., Rosa, D. R. N., Matos, J. X., Inverno, C. M. C., Andersen, T., 2013. Geology of the Rosário-Neves Corvo antiform IPB Portugal: New insights from physical volcanology palynostratigraphy and isotope geochronology studies. *Miner Deposits* 48, 6, 749-766. <https://doi.org/10.1007/s00126-012-0453-0>.

Oliveira, V., 1984. Contribuição para o conhecimento geológico-mineiro da região Alandroal-Juromenha (Alto Alentejo). *Studies, Notes and Works. Mining Development Services, Lisbon*, XXVI (1-4), 103-126.

Oliveira, V., 1986. Prospeção de Minérios Metálicos a Sul do Tejo 1. *Geosciences, Chapters 1-2*, 15-22.

Ordoñez-Casado, B., Gebauer, D., Eguíluz, L., 2009. Zircon Ion-Probe Dating the Maximum Age of Deposition of the Montemolín Succession (Lower Série Negra) in the Ossa Morena Zone, Spain. *Macla* 11, 137-138.

Pasava, J., Kříbek, B., Žák, K., Vymazalová, A., Hailing, D., Taiyi, L., Chaoyang, L., Mingguo, Z., 2004. New data on the origin of Lower Cambrian Mo-Ni-PGE black shales in Guizhou Province, south China. *In: Proceedings of the 32nd IGC*, 877, 189-215.

Pasava, J., Kříbek, B., Vymazalová, A., Sýkorová, I., Žák, K., Orberger, B., 2008. Multiple Sources of Metals of Mineralization in Lower Cambrian Black Shales of South China: Evidence from Geochemical and Petrographic Study. *Resource Geology* 58, 25-42.
<https://doi.org/10.1111/j.1751-3928.2007.00042.x>.

Peltola, E., 1968. On some geochemical features in the black schists of the Outokumpu area, Finland: *Geology Society Finland Bulletin* 40, 39-50.

Perdigão, J. C., Oliveira, J. T., Ribeiro, A., 1982. Explanatory notice of sheet 44-B (Barrancos) of the Geological Map of Portugal at scale 1:50 000. *Geological Surveys of Portugal*.

Pereira, M. F., Apraiz, A., Chichorro, M., Silva, J. B., Armstrong, R. A., 2010. Exhumation of high-pressure rocks in northern Gondwana during the Early Carboniferous (Coimbra–Cordoba shear zone, SW Iberian Massif): Tectonothermal analysis and U–Th–Pb SHRIMP in-situ zircon geochronology. *Gondwana Research* 17, 440-460. <https://doi.org/10.1016/j.gr.2009.10.001>.

Pereira, M. F., Chichorro, M., Linnemann, U., Eguíluz, L., Silva, J. B., 2006. Inherited arc signature in Ediacaran and Early Cambrian basins of the Ossa-Morena Zone (Iberian Massif, Portugal): paleogeographic link with European and North African Cadomian correlatives. *Precambrian Research* 144, 297-315. <https://doi.org/10.1016/j.precamres.2005.11.011>.

Pereira, M. F., Silva, J. B., Chichorro, M., Ordóñez-Casado, B., Lee, J. K. W., Williams, I. S., 2012b. Early Carboniferous wrenching, exhumation of high-grade metamorphic rocks and basin in-stability in SW Iberia: constraints derived from structural geology and U–Pb and ^{40}Ar – ^{39}Ar geochronology. *Tectonophysics* 558-559, 28-44. <https://doi.org/10.1016/j.tecto.2012.06.020>.

Pereira, M. F., Solá, A. R., Chichorro, M., Lopes, L., Gerdes, A., Silva, J. B., 2012a. North-Gondwana assembly, break up and paleogeography: U–Pb isotope evidence from detrital and igneous zircons of Ediacaran and Cambrian rocks of SW Iberia. *Gondwana Research* 22 (3-4), 866-881. <https://doi.org/10.1016/j.gr.2012.02.010>.

Perkins, R. B., Mason, C. E., 2015. The relative mobility of trace elements from short-term weathering of a black shale. *Applied Geochemistry* 56, 67-79. <http://dx.doi.org/10.1016/j.apgeochem.2015.01.014>.

Perkins, R.B., Foster, A.L., 2004. Mineral affinities and distribution of selenium and other trace elements in black shales and phosphorites of the Phosphoria Formation. In: Hein, J. R. (Eds.), *Life Cycle of the Phosphoria Formation: From Deposition to the Post-mining Environment*, Elsevier, Amsterdam, 251-295. [https://doi.org/10.1016/S1874-2734\(04\)80012-3](https://doi.org/10.1016/S1874-2734(04)80012-3).

Peters, K. E., Walters, C. C., Moldowan, J. M., 2005. *The Biomarker Guide*, 2nd edition. Cambridge University Press, 1155 pp. <https://doi.org/10.1017/S0016756806212056>.

Petersen, H. I., Schovsbo, N. H., Nielsen, A. T., 2013. Reflectance measurements of zooclasts and solid bitumen in Lower Paleozoic shales, southern Scandinavia: Correlation to vitrinite reflectance. *International Journal of Coal Geology* 114, 1-18. <http://dx.doi.org/10.1016/j.coal.2013.03.013>.

- Pfefferkorn, H. W., 1968. Geologie des Gebietes zwischen Serpa und Mértola (Baixo Alentejo, Portugal). *Munstersche Forschungen zur Geologieund Palaontologie* 9, 1-143.
- Pi, D. H., Jiang, S. Y., Luo, L., Yang, J. H., Ling, H. F., 2014. Depositional environments for stratiform witherite deposits in the Lower Cambrian black shale sequence of the Yangtze Platform, southern Qinling region, SW China: evidence from redox-sensitive trace element geochemistry. *Palaeogeography, Palaeoclimatology, Palaeoecology* 398, 125-131. <https://doi.org/10.1016/j.palaeo.2013.09.029>.
- Pi, D. H., Liu, C. Q., Shields-Zhould, G. A., Jiang, S. Y., 2013. Trace and rare earth element geochemistry of black shale and kerogen in the early Cambrian Niutitang Formation in Guizhou province. South China: Constraints for redox environments and origin of metal enrichments. *Precambrian Research* 225, 218-229. <https://doi.org/10.1016/j.precamres.2011.07.004>.
- Piçarra, J. M., 2000. Estudo estratigráfico do sector de Estremoz - Barrancos, Zona de Ossa Morena, Portugal. PhD thesis, Volume I and II, 268 pp.
- Piercey, S. J., Gibson, H. L., Tardif, N., Kamber, B. S., 2016. Ambient Redox and Hydrothermal Environment of the Wolverine Volcanogenic Massive Sulfide Deposit, Yukon: Insights from Lithofacies and Lithogeochemistry of Mississippian Host Shales. *Economic Geology* 111, 1439-1463. <https://doi.org/10.2113/econgeo.111.6.1439>.
- Pipper, D. Z., 1974. Rare earth elements in the sedimentary cycle: A summary. *Chemical Geology* 14, 285-304. [https://doi.org/10.1016/0009-2541\(74\)90066-7](https://doi.org/10.1016/0009-2541(74)90066-7).
- Pohl, W.L., 2011. *Economic Geology Principles and Practice*. Wiley Blackwell John Wiley and Sons, New York, 688 pp.
- Potter, P. E., Maynard, J. B., Pryor, W. A., 1980. *Sedimentology of Shale. Study Guide and Reference Source*, Springer Verlag, 310 pp. <http://dx.doi.org/10.1007/978-1-4612-9981-3>.
- Quesada, C., 1990. Precambrian terranes in the Iberian Variscan foldbelt. *In: Strachan, R. A., Taylor, G. K., (Eds), Avalonian and Cadomian Geology of the North Atlantic*. Blackie and Sons, Oxford, 109-133.
- Quesada, C., Oliveira, J. T., 2019. *The Geology of Iberia: A Geodynamic Approach, Volume 2: The Variscan Cycle*. Springer International Publishing, 544 pp.
- Ramos, V., Guedes, A., Noronha, F., Dolgopoleva, A., Seltmann, R., Armstrong, R., Stanley, C., Simons, B., Andersen, J., Rollinson, G., 2017. Sn mineralization in W skarns

from “Douro Scheelite Belt”: the example of Tabuaço (Portugal). XII National Congress and XI Iberian of Geochemistry, Books of Abstracts, 24-28.

Reynaud, J. Y., Trentesaux, A., El Albani, A., Aubineau, J., Ngombi-Pemba, L., Guiyeligou, G., Bouton, P., Gauthier-Lafaye, F. and Weber, F., 2018. Depositional setting of the 2.1 Ga Francevillian macrobiota (Gabon): Rapid mud settling in a shallow basin swept by high-density sand flows. *Sedimentology* 65, 670-701. <https://doi.org/10.1111/sed.12398>.

Reinhard, C. T., Planavsky, N. J., Robbins, L. J., Partin, C. A., Gill, B. C., Lalonde, S. V., Bekker, A., Konhauser, K. O., Lyons, T. W., 2013. Proterozoic ocean redox and biogeochemical stasis. *Earth, Atmospheric, and Planetary Sciences* 110 5357-5362. <https://doi.org/10.1073/pnas.1208622110>.

Ribeiro, A., Munhá, J., Dias, R., Mateus, A., Pereira, E., Ribeiro, M. L., Fonseca, P., Araújo, A., Oliveira, T., Romão, J., Chaminé, H., Coke, C., Pedro J., 2007. Geodynamic evolution of SW Europe Variscides. *Tectonics* 26, TC6009. <https://doi.org/10.1029/2006TC002058>.

Ribeiro, A., Munhá, J., Mateus, A., Fonseca, P., Pereira, E., Noronha, F., Romão, J., Rodrigues, J. F., Castro, P., Meireles, C., Ferreira, N., 2009. Mechanics of thick-skinned Variscan overprinting of Cadomian basement (Iberian Variscides). *Comptes Rendus Geoscience* 341 (2-3), 127-139.

Ribeiro, A., Quesada, C., Dallmeyer, R. D., 1990. Geodynamic Evolution of the Iberian Massif. In: Dallmeyer, R.D., Garcia, E.M. (Eds), *Pre-Mesozoic Geology of Iberia*. IGCP-Project 233. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-83980-1_28.

Rimstidt, J. D., Chermak, J. A., Schreiber, M. E., 2017. Processes that control mineral and element abundances in shales. *Earth-Science Reviews* 171, 383-399. <https://doi.org/10.1016/j.earscirev.2017.06.010>.

Rimmer, S. M., 2004. Geochemical paleoredox indicators in Devonian-Mississippian black shales, Central Appalachian Basin (USA). *Chemical Geology* 206, 373-391. <https://doi.org/10.1016/j.chemgeo.2003.12.029>.

Robardet, M., Gutiérrez-Marco, J.C., 2004. The Ordovician, Silurian and Devonian sedimentary rocks of the Ossa-Morena Zone (SW Iberian Peninsula, Spain). *Journal of Iberian Geology* 30, 73-92.

- Robb, L. J., 2005. Introduction to Ore-Forming Processes. Blackwell Science Ltd, 373 pp.
- Roseiro, J., Moreira, N., Nogueira, P., Maia, M., Araújo, A., Pedro, J., 2020. Depositional environment and passive-to-active margin transition as recorded by trace elements chemistry of lower-middle Palaeozoic detrital units from the Ossa-Morena Zone (SW Iberia). *Geological Communications* 107 (II), 39-46.
- Ross, D. J. K., Bustin, R. M., 2006. Sediment geochemistry of the Lower Jurassic Gordondale Member, northeastern British Columbia. *Bulletin of Canadian Petroleum Geology* 54, 337-365.
- Ross, D. J. K.; Bustin, R. M., 2009. Investigating the use of sedimentary geochemical proxies for paleoenvironment interpretation of thermally mature organic-rich strata: Examples from the Devonian-Mississippian shales, Western Canadian Sedimentary Basin. *Chemical Geology* 260, 1-19. <https://doi.org/10.1016/j.chemgeo.2008.10.027>.
- Rudnick, R. L., Gao, S., 2014. Composition of the continental crust. *Treatise on Geochemistry*, 2nd edition, Elsevier 3, 1-64. <https://doi.org/10.1016/B0-08-043751-6/03016-4>.
- Sáez, R., Moreno, C., González, F., 2011. Black shales and massive sulfide deposits: causal or casual relationships? Insights from Rammelsberg, Tharsis, and Draa Sfar. *Miner Deposita* 46, 585-614. <https://doi.org/10.1007/s00126-010-0311-x>.
- Sánchez-Lorda, M. E., Ábalos, B., García de Madinabeitia, S., Eguíluz, L., Gil Ibarguchi, J. I., Paquette, J. L., 2016. Radiometric discrimination of pre-Variscan amphibolites in the Ediacaran Serie Negra (Ossa-Morena Zone, SW Iberia). *Tectonophysics* 681, 31-45.
- Sánchez-Lorda, M. E., Sarrionandia, F., Ábalos, B., Carracedo, M., Eguíluz, L., Gil Ibarguchi, J. I., 2014. Geochemistry and paleotectonic setting of Ediacaran metabasites from the Ossa-Morena Zone (SW Iberia). *International Journal of Earth Sciences* 103, 1263-1286. <https://doi.org/10.1007/s00531-013-0937-x>.
- Schäfer, H. J., Gebauer, D., Nagler T. F., Eguíluz, L., 1993. Conventional and ion-microprobe U-Pb dating of detrital zircons of the Tentudía Group (Serie Negra, SW Spain): implications for zircon systematics, stratigraphy, tectonics and the Precambrian/Cambrian boundary. *Contributions to Mineralogy and Petrology* 113, 3, 289-299.

- Schermerhorn, L. J. G., Priem, H. N. A., Boelrijk, N. A. I. M., Hebeda, E. H., Verdurmen, E. A. T., Verschure, R. H., 1978. Age and Origin of the Messejana Dolerite Fault-Dike System (Portugal and Spain) in the Light of the Opening of the North Atlantic Ocean. *The Journal of Geology* 86 (3), 299-309. <https://doi.org/10.1086/649692>.
- Schieber, J., 1978. Black shales. *In: Sedimentology. Encyclopedia of Earth Science*. Springer, Berlin, Heidelberg.
- Semtner, A. K., Klitzsch, E., 1994. Early Paleozoic paleogeography of the northern Gondwana margin: new evidence for Ordovician-Silurian glaciation. *Geologische Rundschau* 83, 743-751. <https://doi.org/10.1007/BF00251072>.
- Shaw, T. J., Geiskes, J. M., Jahnke, R. A., 1990. Early diagenesis in differing depositional environments: the response of transition metals in pore water. *Geochimica et Cosmochimica Acta* 54, 1233-1246. [https://doi.org/10.1016/0016-7037\(90\)90149-F](https://doi.org/10.1016/0016-7037(90)90149-F).
- Sillitoe, R. H., 2005. Supergene Oxidized and Enriched Porphyry Copper and Related Deposits. *Economic Geology* 100, 723-768.
- Silva, A. F., 2005. Litoestratigrafia e estrutura do Supergrupo Dúrico-Beirão (Complexo Xisto-Grauváquico), em Portugal, e a sua correlação com as correspondentes sucessões em Espanha. Instituto Nacional de Engenharia, Tecnologias e Inovação, 2-26.
- Silva, E. A., Miranda, J. M., Luis, J. F., Galdeano, A., 2000. Correlation between the Palaeozoic structures from West Iberian and Grand Banks margins using inversion of magnetic anomalies, *Tectonophysics* 321, 57-71. [https://doi.org/10.1016/S0040-1951\(00\)00080-9](https://doi.org/10.1016/S0040-1951(00)00080-9).
- Sousa, M. B., 1979. O Complexo Xisto-Grauváquico do Douro: Caraterísticas litoestratigráficas. *Memórias e Notas do Museu de Geologia da Universidade de Coimbra*, 31-37.
- Sousa, M., 1982. Litoestratigrafia e estrutura do Complexo Xisto- Grauváquico Ante-Ordovícico - Grupo do Douro (nordeste de Portugal). PhD thesis, University of Coimbra, 222 pp.
- Sousa, M., Sequeira, A., 1989. Carta Geológica de Portugal na escala 1/50 000 e Notícia Explicativa de Folha 10-D (Alijó), Lisboa: Serviços Geológicos de Portugal, 59 pp.
- Sozinov, N. A., 1982. Ore potential of Precambrian black shale formation. *Revista Brasileira de Geociências* 12 (1-3), 506-509.

Spirakis, C. S., Heyl, A. V., 1988. Possible effects of thermal degradation of organic matter on carbonate paragenesis and fluorite precipitation in Mississippi Valley-type deposits. *Geology* 16, 117-1120.

Suárez-Ruiz, I., Flores, D., Mendonça Filho, J. G., Hackley, P. C., 2012. Review and update of the applications of organic petrology: Part 2, Geological and Multidisciplinary Applications. *International Journal of Coal Geology* 98, 73-94. <https://doi.org/10.1016/j.coal.2012.03.005>.

Swaine, D. J., 1990. *Trace Elements in Coal*. Butterworths, London, 278 pp.

Swanson, V. E., 1961. Geology and geochemistry of uranium in marine black shales - a review: U.S. Geological Survey 356-C, 67-112.

Taylor, G. H., Teichmüller, M., Davis, A., Diessel, C. F. K., Littke, R., Robert, P., 1998. *Organic Petrology*. Gebrüder Borntraeger, Berlin, 704 pp.

Taylor, S. R., McLennan, S. M., 1985. *The Continental Crust: its Composition and Evolution*. Blackwell Scientific Publications, Oxford.

Tissot, B., Welte, D. H., 1984. *Petroleum Formation and Occurrence*, 2nd edition. Springer-Verlag, Heidelberg, 669 pp.

Tornos, F., Casquet, C., Relvas, J., Barriga, F., Sáez, R., 2002. Transpressional tectonics and ore deposit formation: the southwestern margin of the Iberian Variscan Belt. *In*: Blundell, D., Neubauer, F., Von Quadt, A., (Eds). *The timing and location of major ore deposits in an evolving orogen*. Geological Society of London, Special Publications 206, 179-198.

Tornos, F., Inverno, C. M. C., Casquet, C., Mateus, A., Ortiz, G., Oliveira, V., 2004. The metallogenic evolution of the Ossa-Morena Zone. *Journal of Iberian Geology* 30, 143-181.

Tourtelot, B., 1979. Black shale: its deposition and diagenesis. *Clays and Clay Mineralogy*, 27, 313-321. <https://doi.org/10.1346/CCMN.1979.0270501>.

Trabucho-Alexandre, J., 2014. More gaps than shale: erosion of mud and its effect on preserved geochemical and palaeobiological signals. *Geological Society of London, Special Publication* 404 (1), 251 p. <https://doi.org/10.1144/SP404.10>.

- Tribouillard, N., Algeo, T. J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. *Chemical Geology* 232, 12-32. <https://doi.org/10.1016/j.chemgeo.2006.02.012>.
- Tuttle, M. L. W., Breit, G. N., Goldhaber, M. B., 2009. Weathering of the New Albany Shale, Kentucky: II. Redistribution of minor and trace elements. *Applied Geochemistry* 24, 1565-1578. <https://doi.org/10.1016/j.apgeochem.2009.04.034>.
- Ugidos, J. M., 1990. Granites as a paradigm of genetic processes of granitic rocks: I-types vs S-types.
- US - EPA, 2002. Methods for the determination of Total Organic Carbon (TOC) in soils and sediments. United States Environmental Protection Agency (U. S. EPA), Office of Research and Development, National Exposure Research Laboratory, Las Vegas, NV. NCEA-C-1282, EMASC-001, 26 pp.
- Vegas, K., 1968. Sobre la existencia de Precámbrico en la Baja Extremadura. *Estudios Geológicos*, 24, 85-89.
- Velasco, F., Herrero, J. M., Suárez, S., Yusta, I., Alvaro, A., Tornos, F., 2013. Supergene features and evolution of gossans capping massive sulphide deposits in the Iberian Pyrite Belt. *Ore Geology Reviews* 53, 181-203. <http://dx.doi.org/10.1016/j.oregeorev.2013.01.008>.
- Vine, J. D., Tourtelot, E. B., 1970. Geochemistry of black shale deposits - a summary report: *Economic Geology* 65, 253-272. <http://dx.doi.org/10.2113/gsecongeo.65.3.253>.
- Wang, N., Li, M., Hong, H., Song, D., Tian, X., Liu, P., Fang, R., Chen, G., Wang, M., 2019. Biological sources of sedimentary organic matter in Neoproterozoic–Lower Cambrian shales in the Sichuan Basin (SW China): Evidence from biomarkers and microfossils. *Palaeogeography, Palaeoclimatology, Palaeoecology* 516, 342-353. <https://doi.org/10.1016/j.palaeo.2018.12.012>.
- Wang, Y., Chen, J., Shen, W., Min Li., 2022. Mechanism of Organic Matter Accumulation in Black Shales of the Yuertusi Formation in the Tarim Basin: Insights From Paleoenvironmental Variation During the Early Cambrian. *Frontiers in Earth Science* 10. <https://doi.org/10.3389/feart.2022.879658>.
- Wedepohl, K. H., 1971. Environmental influences on the chemical composition of shales and clays. *Physics and Chemistry of the Earth* 8, 305-333. [https://doi.org/10.1016/0079-1946\(71\)90020-6](https://doi.org/10.1016/0079-1946(71)90020-6).

Wignall, P. B., 1994. *Black Shales*. Oxford, England. Clarendon Press, 127 pp.

Wilde, P., Quinby-Hunt, M. S., Erdtmann, B., 1996. The whole-rock cerium anomaly: a potential indicator of eustatic sea-level changes in shales of the anoxic facies. *Sedimentary Geology* 101, 1-2, 43-53. [https://doi.org/10.1016/0037-0738\(95\)00020-8](https://doi.org/10.1016/0037-0738(95)00020-8).

Wright, J., Schrader, H., Holser, W. T., 1987. Paleoredox variations in ancient oceans recorded by rare earth elements in fossil apatite. *Geochimica et Cosmochimica Acta* 51, 631-644. [https://doi.org/10.1016/0016-7037\(87\)90075-5](https://doi.org/10.1016/0016-7037(87)90075-5).

Xu, G., Lin, X., 2000. Geology and geochemistry of the Changlongshan skarn iron deposit, Anhui Province, China. *Ore Geology Reviews* 16, 91-106. [https://doi.org/10.1016/S0169-1368\(99\)00025-6](https://doi.org/10.1016/S0169-1368(99)00025-6).

Yanyun Xiong, Taofa Zhou, Yu Fan, Jing Chen, Biao Wang, Jun Liu, Fangyue Wang, 2022. Enrichment mechanisms and occurrence regularity of critical minerals resources in the Yaojialing Zn skarn polymetallic deposit, Tongling district, eastern China, *Ore Geology Reviews* 144, 104822. <https://doi.org/10.1016/j.oregeorev.2022.104822>.

Zheng, W., Tang, J., Zhong, K., Ying, L., Leng, Q., Ding, S., Lin, B., 2016. Geology of the Jiama porphyry copper–polymetallic system, Lhasa Region, China, *Ore Geology Reviews* 74, 151-169. <https://doi.org/10.1016/j.oregeorev.2015.11.024>.