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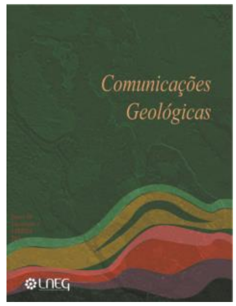
Depositional environment and passive-to-active margin transition as recorded by trace elements chemistry of lower-middle Palaeozoic detrital units from the Ossa-Morena Zone (SW Iberia)



Ambiente deposicional e transição margem ativa-passiva registada no quimismo de elementos traço em unidades detríticas do Paleozóico inferior-médio na Zona de Ossa-Morena (SW Ibérico)

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Abstract: New lithogeochemical data of Lower-Middle Palaeozoic metasedimentary rocks of the Ossa-Morena Zone are here presented and integrated with previously published data, as well as a discussion on their provenance and geotectonic settings. In the Cambrian – Lower Ordovician rift stages, metasediments mostly derived from an acid continental source with passive margin geochemical affinities, showing a significant recycled sediment component, as well as an oxidizing depositional environment. Metasediments related with the drift stage, during Ordovician and Silurian ages, display general geochemical features similar to those that characterize the Cambrian units, inferring the prevailing acid source and passive margin geotectonic settings, and slightly anoxic depositional conditions in the end of this stage. In turn, geochemistry of samples representative of the Devonian debris deposition contrast with the passive continental margin geochemical data; notwithstanding the dominant acid source, an increased trend for a basic/intermediate sedimentary component can be observed, thus inferring a contribution of an external volcanic (probably subduction-related) source during Devonian ages. These interpretations are in accordance with other studies regarding north Gondwana rift and drift stages during Cambrian-Silurian times and active margin settings during Devonian.

Keywords: Ossa-Morena Zone, sedimentary provenance, detrital units, lithogeochemistry.

Resumo: Novos dados de litogeoquímica referentes às rochas metassedimentares do Paleozóico Inferior-Médio da Zona de Ossa-Morena são aqui apresentados e integrados com dados bibliográficos, assim como uma discussão relativa à sua proveniência e enquadramento geotectónico. Nos estádios de rifting do Câmbrico-Ordovícico Inferior, os metassedimentos derivam de uma fonte ácida continental com afinidades geoquímicas típicas de margem passiva, evidenciando uma componente sedimentar reciclada significativa, assim como um ambiente deposicional oxigenado. A sedimentação nas bacias de estiramento durante o Ordovícico e o Silúrico (fase de *drift*) mostram características geoquímicas semelhantes às sucessões do Câmbrico, inferindo a continuada contribuição de fontes ácidas em ambiente de margem passiva, embora os indicadores geoquímicos de oxidação-redução indiquem um ambiente deposicional relativamente anóxico no final deste estágio. Análises de amostras representativas de deposição detrítica devónica contrastam com os dados referentes às fases anteriores; não obstante a fonte ácida dominante, verifica-se a tendência para uma mistura de componentes sedimentares básicas/intermédias, inferindo a contribuição concomitante de uma fonte externa (possivelmente relacionada com o início do processo de subdução) durante o Devónico. Estas observações estão de acordo com outros estudos referentes aos estágios de *rift* e *drift* durante o Câmbrico-Silúrico e estado de margem ativa durante o Devónico.

Keywords: Zona de Ossa-Morena, proveniência sedimentar, unidades detríticas, litogeoquímica.

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1. Introduction

Trace element geochemical data of detrital rocks provide important tools to study the sedimentary source, depositional environment and tectonic settings of siliciclastic formations in sedimentary basins. This methodological approach is plausible as some trace elements do not tend to fractionate during weathering events, mineral sorting during transport and diagenesis or regional metamorphism (*e.g.* Bathia and Crook, 1986; Floyd and Leveridge, 1987; McLennan, 2001).

In the Ossa-Morena Zone (OMZ, SW Iberia), several metasedimentary rock suites are known to constitute lithostratigraphic successions, representative of sedimentary dynamics from Cambrian to Carboniferous (*e.g.* Oliveira *et al*., 1991; Robardet and Gutierrez Marco, 2004; Araújo *et al*., 2013). Debris deposition in the OMZ is mostly present from Cambrian to Devonian times, therefore chemical imprints on these successions should reflect the changes on the depositional environment; i.e., it is possible to assess their provenance through the main tectonic stages: (1) Cambrian rift events, (2) Ordovician – Lower Devonian drift stage, and (3) Lower Devonian subduction initiation events that culminated in continental collision (Sánchez-García *et al*., 2003, 2008, 2010, 2019; Robardet and Gutierrez Marco, 2004; Ribeiro *et al*., 2007, 2010; Moreira *et al*., 2010, 2014, 2019; Pereira *et al*., 2017).

This work aims to contribute to the knowledge of the geodynamic evolution of the OMZ and the Iberian Variscides, checking previous interpretations and its geodynamic evolution, based on new litogeochemical data.

2. Geological background

The OMZ is a tectono-stratigraphic zone of the Iberian Massif (Julivert *et al.*, 1974), interpreted as a dissociated remnant of the outer belt of the northern Gondwana margin, that comprises a sequence of basins packed with debris resulting from the dismantling of a continental basement (presumably from Gondwana; *e.g.* Dias *et al*., 2016) during the early stages of the Variscan Cycle (Ribeiro *et al*., 2007; Simancas, 2019). These Lower to Middle Palaeozoic suites consist in a succession of metasedimentary rocks, discordantly settled on top of the 'Série Negra' Neoproterozoic basement (*e.g*. Oliveira *et al*., 1991; Piçarra, 2000; Araújo *et al*., 2013; Moreira *et al*., 2014;). Thoroughly studies based on bio- and lithostratigraphic correlations, tectono-metamorphic features, geochronological data and metavolcanic rocks lithogeochemistry (*e.g.* Sánchez-Garcia *et al*., 2003, 2008, 2010, 2019; Robardet and Gutierrez Marco, 2004; Borrego *et al*., 2006; Pereira *et al*., 2006; Araújo *et al.*, 2013) defined and distinguished several Lower to Middle Palaeozoic formations in the Portuguese sectors of the OMZ, which can be organized in a simplified OMZ lithostratigraphic succession, as shown in figure 1.

3. Materials and analytical methods

Eleven OMZ metasedimentary rock samples, representing the Colorada (n = 5; Upper Ordovician), Xistos com Nódulos (n = 4; Silurian), Xistos Raiados (n = 1; Lower Devonian) and Terena (n = 1; Lower Devonian) formations were collected and whole-rock trace element analyses were carried out in ALS laboratories (Sevilla), using the ME-MS81 and ME-4ACD81 analytical packages. Analytical procedures were: i) Li-borate fusion, acid digestion and ICP-MS analysis in ME-MS81, and ii) four acid digestion and ICP-AES analysis in ME-4ACD81. The new data was compared and assembled with previously published data of the Vila Boim, Terrugem, Carvalhal, Colorada, Xistos Raiados and Terena formations (n = 61; Pereira *et al.*, 2006; Borrego, 2009; Cruz, 2013), representing the lithostratigraphic successions from early Cambrian to the Lower Devonian.

4. Results

Trace elements analyses of the sampled OMZ Ordovician - Devonian detrital units are displayed in table1 and C1 chondrite normalized (CN; Palme and O'Neill, 2014) rare-earth elements and North American Shale Composite (NASC; Condie, 1993) normalized trace elements spider diagrams of both analyzed samples and bibliographic data (for comparison) are shown in figure 2. A general geochemical characterization of the new Ordovician - Devonian data are here described (given in average ± standard deviation or ranging minimum - maximum) as well as the geochemical ratios that indicate the most significant elemental features for provenance analysis and paleo-redox conditions studies (*e.g.* Bathia and Crook, 1986; Floyd and Leveridge, 1987; Middleburg *et al*., 1988; Jones and Manning, 1994; Wignall and Twichett, 1996; Hoffman *et al*., 1998; McLennan, 2001).

The Ordovician units, represented by the Colorada Fm. samples, show consistent values between sampled lithotypes (Fig. 2B), with general low values in Sr (0.6 × NASC), Ni (0.7 × NASC), and Pb (0.4 × NASC), but considerable enrichments in W (5.3, up to 19.0 × NASC), U (1.8, up to 3.5 × NASC) and As (1.9, up to 2.5 × NASC). Variations in the Cu content are noticeable, in which greywackes display positive anomalies (3.3 – 3.9 × NASC), whereas in other lithotypes is depleted (0.1 – 0.36 × NASC).

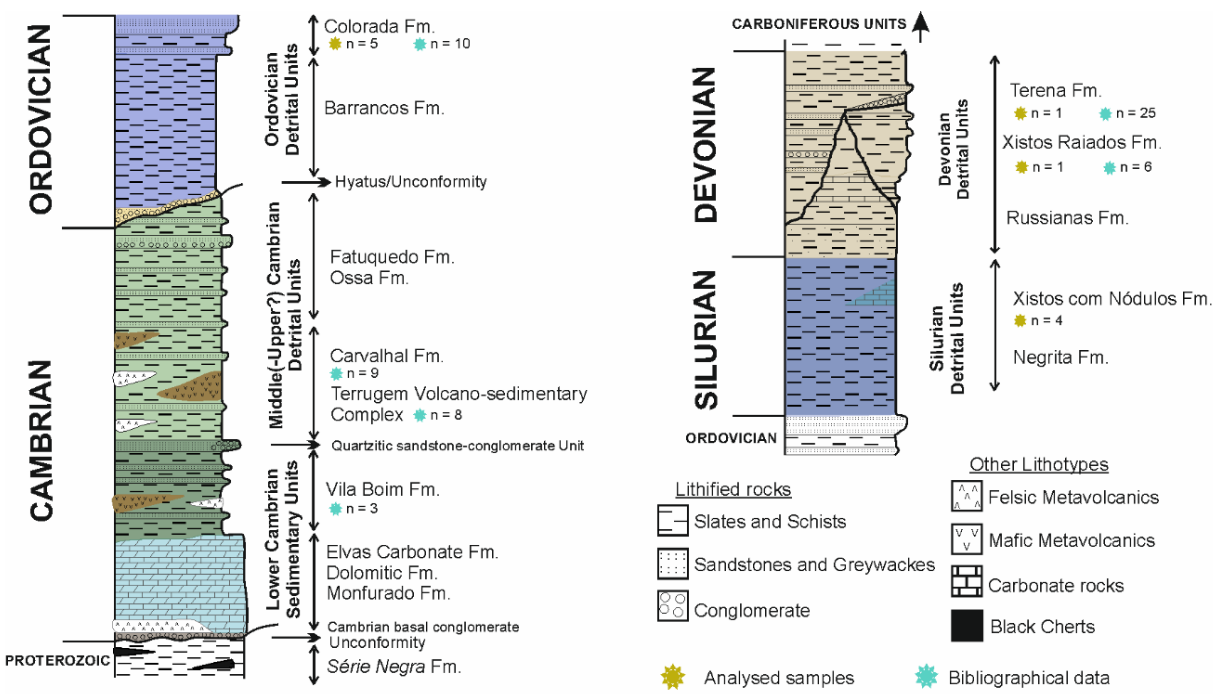


Figure 1. Simplified Ossa-Morena Zone (OMZ) Cambrian-Devonian lithostratigraphic sequence of the different metasedimentary formations (adapted from Oliveira *et al*., 1991; Araújo *et al*., 2013).

Figura 1. Sequência litoestratigráfica simplificada das várias formações metassedimentares da Zona de Ossa-Morena (ZOM) desde o Câmbrico ao Devónico (adaptado de Oliveira *et al*., 1991; Araújo *et al*., 2013).

Table 1. Trace element analyses of different OMZ Palaeozoic metasedimentary formations.

Tabela 1. Análises de elementos traço das diferentes formações metassedimentares do Paleozóico da ZOM.

Ref.	456-01	SD4-01	SD4-02	SD4-09	SD4-16	519-5	518-2	518-3	518-4	519-1	519-6
Unit	Colorada Fm.	Colorada Fm.	Colorada Fm.	Colorada Fm.	Colorada Fm.	Xistos com Nódulos Fm.	Xistos com Nódulos Fm.	Xistos com Nódulos Fm.	Xistos com Nódulos Fm.	Xistos Raiados Fm.	Terena Fm.
Lithotype	Quartzite	Greywacke	Greywacke	Psammite	Schist/Slate	Schist/Slate	Schist/Slate	Schist/Slate	Schist/Slate	Schist/Slate	Greywacke
Ba	679	672	604	830	668	374	509	46	1115	379	426
Sr	157	91	63	69	53	37	133	15	270	156	193
Rb	176	186	162	282	221	106	210	9	271	153	149
Cs	6	6	5	6	7	3	5	0.27	16	6	8
V	119	104	107	95	113	1220	197	360	225	110	224
Co	20	26	16	19	14	1	28	2	<1	11	28
Ni	33	60	55	40	27	19	83	8	1	44	65
Cr	80	80	80	70	90	230	140	30	160	100	150
Zr	165	261	288	257	167	163	187	17	246	94	175
Hf	5	7	7	8.50	5	4	5	0.30	8	3	5
Nb	16	19	20	23	16	11	23	0.80	31	14	25
Ta	1	2	1	2	1	0.70	2	<0.1	2	1	2
Ga	31	24	27	32	25	21	34	3	44	27	42
Mo	0	1	1	0	0	7	0	3	0	0	2
Sn	4	4	4	7	4	2	5	<1	6	3	6
W	4	4	40	4	4	2	4	2	5	3	3
As	<5	52	64	71	26	28	13	28	8	18	24
Pb	18	4	8	4	<2	75	8	<2	<2	8	12
Zn	104	62	83	10	8	37	53	5	9	96	97
Cu	18	166	196	5	12	93	23	57	38	15	21
Th	13	16	17	21	15	8	18	0.47	25	14	20
U	2	3	4	9	6	10	3	2	3	1	3
Y	34	33	37	40	28	53	30	6	58	23	43
Sc	20	13	10	14	15	12	21	2	22	10	23
La	57	52	54	51	44	68	67	3	87	45	76
Ce	107	113	115	110	96	82	126	4	167	87	148
Pr	13	12	12	12	11	14	14	0.69	20	10	17
Nd	47	45	46	44	39	55	51	3	74	37	64
Sm	9	8	9	9	7	9	9	0.68	13	7	12
Eu	2	2	2	2	1	2	2	0.12	2	1	2
Gd	7	6	7	7	6	8	7	0.71	11	5	9
Tb	1	1	1	1	0.92	1	1	0.11	2	0.80	1
Dy	7	6	7	8	5	7	6	0.69	11	5	9
Ho	1	1	1	2	1	2	1	0.15	2	0.84	2
Er	4	3	4	5	3	5	3	0.48	6	2	5
Tm	0.50	0.53	0.52	0.69	0.42	0.73	0.48	0.08	0.79	0.34	1
Yb	4	3	3	4	3	5	3	0.56	5	2	4
Lu	0.57	0.46	0.50	0.56	0.41	0.89	0.54	0.09	0.81	0.34	1

These units also show relatively variable Th/U (4.1 ± 1.7) and Zr/Sc (17.3 ± 8.1), but consistent Ni/Co (2.3 ± 0.1), V/Cr (1.3 ± 0.1), Nb/Ta (13.0 ± 1.3) and La/Th (3.3 ± 0.7) ratios. The CN REE patterns (Fig. 2B) are characterized by high LREE enrichments over HREE ($[La/Sm]_{CN}$ = 3.7 – 4.0; $[La/Yb]_{CN}$ = 8.7 – 11.0; $[Ce/Ce^*]_{CN}$ = 1.0 – 1.1) and significative negative Eu anomaly ($[Eu/Eu^*]_{CN}$ = 0.6 – 0.7).

Analyses of the Silurian Xistos com Nódulos Fm. samples exhibit inconsistent values, and two groups of geochemical features can thus be distinguished (Fig. 2B):

(1) samples enriched in W (1.9 and 2.3 × NASC) but depleted in Cu (0.5 and 0.8 × NASC) and As (0.3 and 0.5 × NASC), with high Th/U (6.3 and 9.1), Nb/Ta (13.3 and 14.2), La/Th (3.5 and 3.8) and Zr/Sc (10.0 and 11.6), but low Ni/Co (up to 3.0) and V/Cr (up to 1.4) ratios, CN REE patterns with high LREE fractionation over HREE ($[La/Sm]_{CN}$ = 4.1 – 4.5; $[Ce/Ce^*]_{CN}$ = 1.0; $[La/Yb]_{CN}$ = 11.1 – 13.5) and negative anomaly in Eu ($[Eu/Eu^*]_{CN}$ = 0.6 and 0.7); and

(2) samples with high enrichments in V (2.3 and 9.4 × NASC), Mo (3.0 and 7.0 × NASC) and, to a lesser extent, Cu (1.1 and 1.9 × NASC), with low Th/U (up to 0.8) ratio, but high Ni/Co (up to 19.0), V/Cr (up to 12.0), Nb/Ta (up to 15.7), La/Th (5.7 and 8.3) and Zr/Sc (8.5 and 13.6). CN REE diagrams are defined by less pronounced fractionation between LREE and HREE ($[La/Sm]_{CN}$ = 2.5 and 4.7; $[La/Yb]_{CN}$ = 3.3 and 8.5), and marked negative Eu and Ce anomalies ($[Eu/Eu^*]_{CN}$ = 0.5 and 0.6; $[Ce/Ce^*]_{CN}$ = 0.6 and 0.7); one of these samples show extreme REE depletion (La = 11.4 × C1; Sm = 4.6 × C1; Yb = 3.5 × C1; figure 2B).

Analyzed Devonian samples show similar geochemical features between them and are represented by samples of the Xistos Raiados Fm. and Terena Fm. For Xistos Raiados Fm. the distinctive chemical features consist in significant depletion in As (0.6 × NASC), Pb (0.4 × NASC) and Cu (0.3 × NASC), high Th/U (11.2), Nb/Ta (12.5) and Zr/Sc (9.4) ratios, and low Ni/Co (4.0), V/Cr (1.1) and La/Th (3.2). The Terena Fm. analysis display enrichments in Mo (2 × NASC), Nb (1.9 × NASC) and V (1.7 × NASC) and noticeable depletion in Cu (0.42 × NASC), high Nb/Ta (13.9) and Zr/Sc (7.6) and low Th/U (5.8), Ni/Co (2.3), V/Cr (1.5) and La/Th (3.8) ratios. CN REE diagrams show similar patterns between both formations (though higher contents in Terena Fm.), with positive enrichments in LREE over flat HREE ($[La/Sm]_{CN}$ = 3.8 – 3.9; $[Ce/Ce^*]_{CN}$ = 1.0; [La/Yb]CN = 11.7 – 13.3), and mild negative Eu anomaly ($[Eu/Eu^*]_{CN}$ = 0.7), as shown in figure 2C.

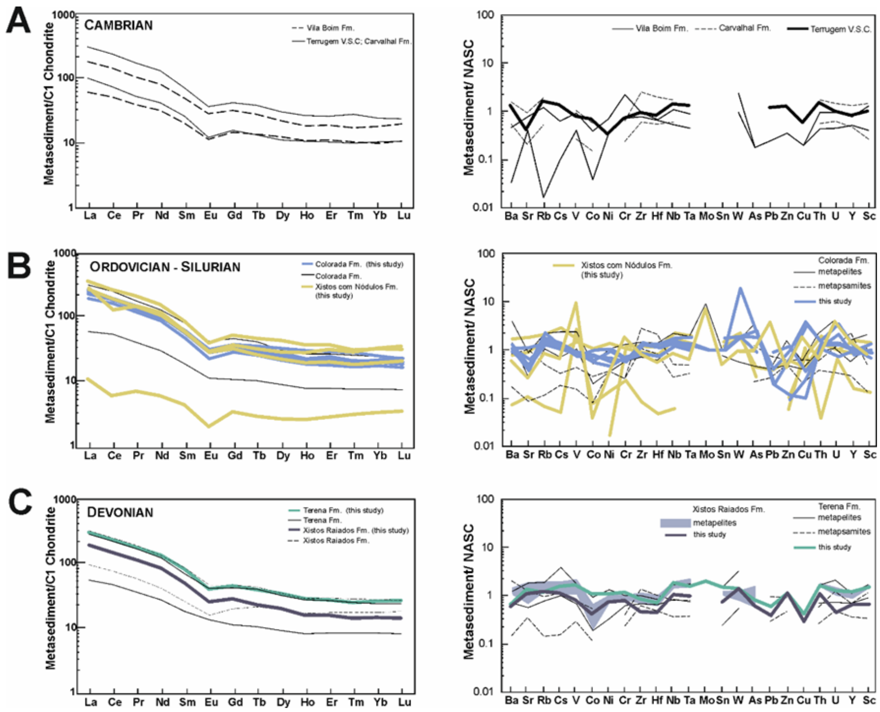


Figure 2. C1 chondrite- and NASC-normalized patterns of trace elements regarding OMZ Cambrian (A), Ordovician, Silurian (B) and Devonian (C) units for both analyzed and bibliographical samples. C1 chondrite values from Palme and O'Neill (2014) and NASC values from Condie (1993). Metasedimentary bibliographical data represents the Vila Boim Fm. (n= 3; Cruz, 2014), Terrugem V.S.C. (n= 1; Cruz, 2014), Carvalhal Fm. (n = 9; Pereira *et al*., 2006), Colorada Fm. (n = 10; Borrego, 2009), Xistos Raiados Fm. (n = 6; Borrego, 2009) and Terena Fm. (n = 25; Borrego, 2009), and exposed data concerns the minimum – maximum range for each formation.

Figura 2. Padrões de elementos traço normalizados ao condrito C1 e ao NASC, relativos às unidades do Câmbrico (A), Ordovícico, Silúrico (B) e Devónico (C) da ZOM, de análises obtidas e publicadas. Valores do condrito C1 retirados de Palme e O'Neill (2014) e valores de NASC retirados de Condie (1993). Dados bibliográficos de análises aos metassedimentos representam a Fm. Vila Boim (n= 3; Cruz, 2014), C.V.S. Terrugem (n= 1; Cruz, 2014), Fm. Carvalhal (n = 9; Pereira *et al*., 2006), Fm. Colorada (n = 10; Borrego, 2009), Fm. Xistos Raiados (n = 6; Borrego, 2009) e Fm. Terena (n = 25; Borrego, 2009), e os dados projectados correspondem aos valores mínimo – máximo de cada formação.

5. Discussion

5.1. Provenance and depositional tectonic environment

Analyzed samples were assembled with published data regarding Cambrian (Fig. 2A), Ordovician, Silurian (Fig. 2B) and Devonian (Fig. 2C) units in order to have a wider insight of the evolution of the OMZ detrital successions during the Variscan Cycle, namely from the passive margin stages until the initiation of the active margin phase. Data from this study are congruent with published data, as observed in the trace elements patterns (Fig. 2).

Some trace elements do not tend to fractionate during sedimentation and regional metamorphism, thus considered immobile, and therefore, elemental ratios can be used to distinguish the dominant sources in provenance studies (*e.g.* Bathia and Crook, 1986; Floyd and Leveridge, 1987; Middleburg *et al.*, 1988; McLennan, 2001). Features in the chondrite normalized REE patterns in all studied OMZ detrital units suggest a dominant felsic continental source (Middelburg *et al*., 1988) for the different formations, with higher LREE over the HREE and a slightly marked Eu negative anomaly (Fig. 2). Exception of the typical patterns is observed on two analyses of the Xistos com Nódulos Fm. samples, that also have a noticeable negative Ce anomaly (Fig. 2B).

Also, the immobile elements content and their relationships (mainly La, Eu/Eu*, Th, Zr, Hf and Sc, as shown in geotectonic diagrams of Figs. 3 and 4A, B) enable to assign the studied samples to their tectonic environment:

i) metasedimentary successions with ages ranging from Cambrian to Silurian are apparently derived from an acid continental source (continental margin – continental island arc?), showing passive margin chemical affinities with ancient sediments (Fig. 3A, B) inferring an increase in the coarser debris component (presumably zircon), while
ii) Lower Devonian detrital rocks chemistry suggests a tenuos mixed acid/basic source contribution (Fig. 3C; Bathia and Crook, 1986; Floyd and Leveridge, 1987; Middleburg et al., 1988).

5.2. Monitoring paleoredox conditions

Several trace element ratios of sedimentary rocks have also been successfully combined and used as proxies for indicating redox depositional conditions of ancient sedimentary rocks (*e.g.* Jones and Manning, 1994; Wignall and Twichett, 1996; Hoffman *et al.*, 1998; Rimmer, 2004; Jorge *et al*., 2006; Tribovillard *et al*., 2006; Sáez *et al.*, 2011; Georgiev *et al.*, 2012; Holmden *et al*., 2015; Piercey *et al*., 2016; Luz and Mateus, 2019), thus inferring the degree of oxygenation or anoxia in the sediment - bottom-waters interface. The oxic-anoxic variations in different formations are thought to be essentially controlled by oxygen and sulphur availability, mainly represented by organic matter and sulphides (*e.g.* Jones and Manning, 1994).

Oxidizing (to suboxic) depositional environment of OMZ Cambrian - Devonian detrital units appeared to have been monotonous, with some exceptions observed in the Xistos com Nódulos Fm. samples, that suggest a transition to an anoxic environment during Silurian (*e.g.* Fig. 4C, D, E; Tab. 1); to a lesser extent, the Colorada Fm. samples also show evidences of reduced conditions.

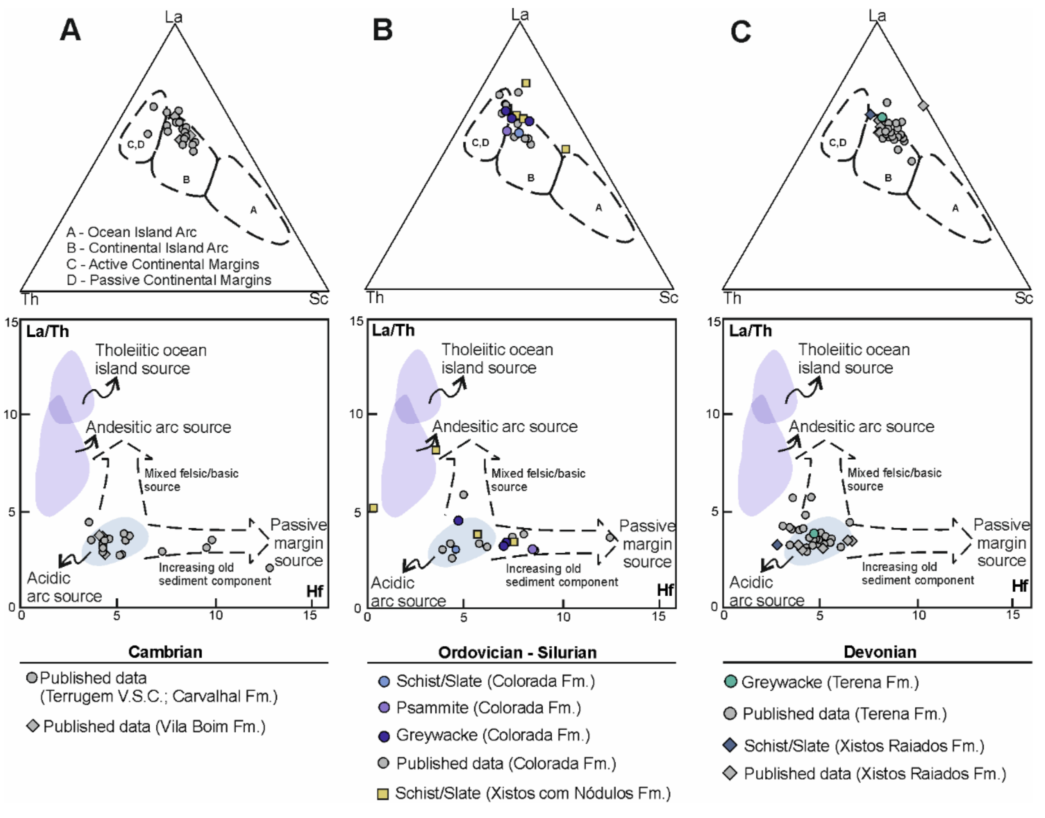
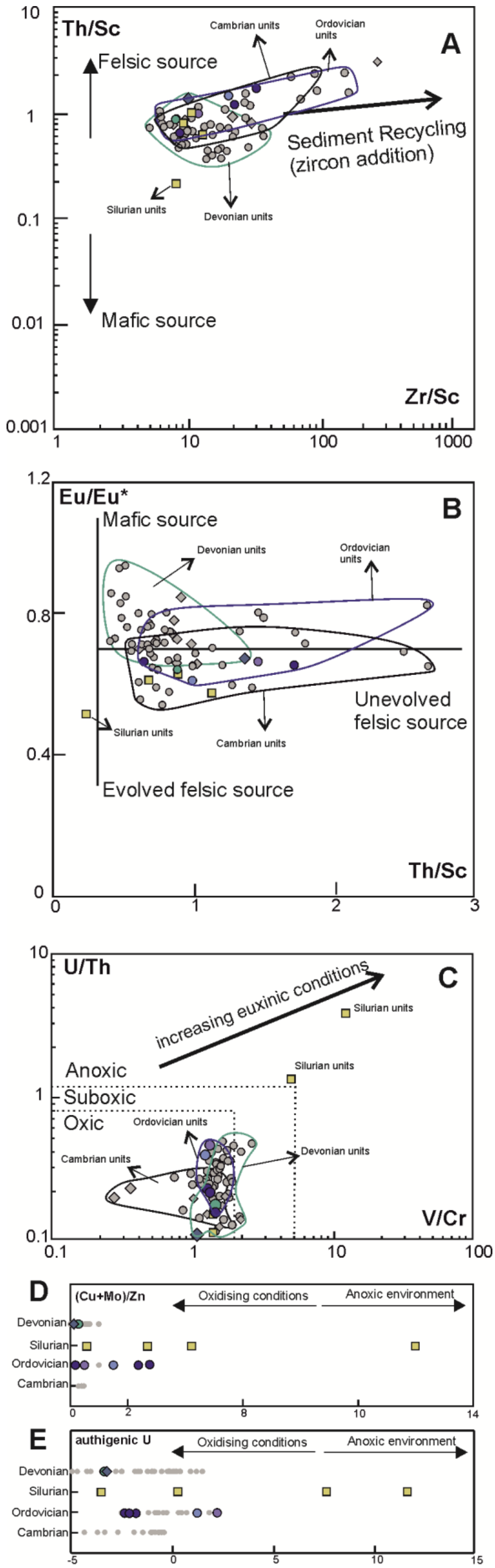


Figure 3. Discrimination tectonic diagrams for the different OMZ metasedimentary units regarding the Cambrian (A), Ordovician, Silurian (B) and Devonian (C) analyses. Ternary La-Th-Sc diagram adapted from Bhatia and Crook (1986) and La/Th-Hf diagram from Floyd and Leveridge (1987).

Figura 3. Diagramas discriminantes de ambientes tectónicos deposicionais para as diferentes unidades metassedimentares da ZOM, relativas a análises das unidades do Câmbrico (A), Ordovícico, Silúrico (B) e Devónico (C). Diagrama ternário La-Th-Sc adaptado de Bhatia e Crook (1986) e diagrama La/Th-Hf de Floyd e Leveridge (1987).



In less oxidizing conditions, reduced vanadium can be incorporated in organic matter lattice and concentrated in sediments deposited in such conditions, while chromium is withheld in the clastic fraction; this way, it is considered that V/Cr > 2 ratios are typical of anoxic conditions, whereas V/Cr ≈1 ratios should represent the O – H_2S interface in sediments (Jones and Manning, 1994). The higher Ni/Co and (Cu+Mo)/Zn ratios (Hallberg, 1976; 1982; Fig. 4D) in Ordovician-Silurian samples suggest the presence of sulphur species (HS, H_2S) in bottom-waters and diagenetic sulphide (pyrite) deposition in anoxic conditions, as well as favoring conditions to promote copper and molybdenium precipitation over zinc (Jones and Manning, 1994; Tribovillard *et al*., 2006). Moreover, higher molybdenium values in metasediments have been proposed to indicate areas of basins that are submerged by anoxic waters (*e.g.* Rimmer, 2004; Tribovillard *et al*., 2006), however, such theoretical concerns do not mean sulphide-rich zones, but favorable fractionation settings for copper and molybdenium. The increase in authigenic uranium (U-[Th/3]) represents the reduction of soluble oxidized uranium in detrital and organic-rich lithotypes, and consequent precipitation (Fig. 4E). In addition, the negative cerium anomaly in some samples (Fig. 2B) can be an indicator of the reduction of Ce^{4+} to soluble Ce^{3+}, as proposed by German and Elderfield (1990).

These inferences on paleoredox depositional conditions are compatible with previous works regarding OMZ bio- and lithostratigraphic units, which suggest an increase on organic matter components in Xistos com Nódulos Fm. lithotypes and an euxinic depositional environment during the Silurian (*e.g.* Piçarra, 2000; Laranjeira *et al*., 2019).

5.3. Geodynamic considerations

The provenance of Cambrian-Silurian sediments can be attributed to the progressive dismemberment of a felsic continental basement, from the northern rim of Gondwana (which includes the Cadomian arc; Pereira *et al*., 2006; Dias *et al*., 2016) while the Lower Devonian units suggest a transitional deposition environment, from a passive margin to an active tectonic setting, possibly with disparate sedimentary sources.

The numerous paleoredox proxies infer the progressive water-column stratification from Lower Palaeozoic ages (Cambrian-Ordovician oxic and suboxic conditions) through the final passive margin stage (mainly represented by the Xistos com Nódulos Fm. Silurian samples), characterized by the anoxic (to euxinic) sedimentation environment. The Lower Devonian sedimentation tracks the beginning of the active margin processes (*e.g.* Ribeiro *et al*., 2010; Silva *et al*., 2011; Moreira *et al*., 2014), and increase mixing of the water column, thus promoting the oxygenation of the bottom-waters, as reflected by the differences in the Xistos Raiados Fm. and Terena Fm. redox proxies.

New geochemical data here presented, regarding OMZ Palaeozoic detrital units, supports and agrees with previous works (*e.g.* Piçarra, 2000; Borrego *et al*., 2006; Moreira *et al*., 2010; Laranjeira *et al*., 2019;), supporting geodynamic models that proposed subduction initiation in SW Iberian Variscides during Lower Devonian ages (*e.g.* Ribeiro *et al*., 2010; Silva *et al*., 2011; Moreira *et al*., 2014; Moreira and Machado, 2019).

Figure 4. Discriminative diagrams regarding geochemical affinities and recycled components (A and B; adapted from McLennan *et al*., 1990), as well as paleo-redox conditions (C, D and E; adapted from Jones and Manning, 1994; Piercey *et al*., 2016). Symbols as in figure 3.

Figura 4. Diagramas discriminantes referentes às afinidades geoquímicas e componentes recicladas (A e B; adaptado de McLennan *et al*., 1990), assim como as condições paleo-redox de deposição (C, D e E; adaptado de Jones e Manning, 1994; Piercey *et al*., 2016). Simbologia como na figura 3.

6. Conclusion and final remarks

Trace elements relationships of the detrital successions of the OMZ reveal that the different formations derive mostly from an acid continental source, though with particular features that suggest mixed sedimentary components: Cambrian, Ordovician and Silurian chemistry show significant influences typical of passive margin sedimentation (high resistate/recycled constituents), while Devonian samples appear to have a slight volcanic arc contribution (subduction related), with an increase in basic/intermediate components, which may indicate a transition on the tectonic environment, during their deposition.

Regarding the geotectonic setting, ante-Devonian variscan formations are interpreted as representing debris deposition, derived from the progressive dismantling of a continental basement, in trailing edge basins formed during the lower Cambrian crustal thinning episode (*e.g.* Sánchez-Garcia *et al*., 2008, 2010; Moreira *et al*., 2014). Contrastingly, Devonian units correspond to metasedimentary rocks with an apparent contribution from a dismembered (basic-intermediate) volcanic arc, evidencing the active margin of the OMZ during this period, which is in accordance with previous models for the OMZ geodynamic evolution (Ribeiro *et al*., 2010; Silva *et al*., 2011; Moreira *et al*., 2014; Moreira and Machado, 2019). In addition, analyses on paleoredox geochemical tracers suggest a considerable oxidizing (to suboxic) condition during Cambrian, Ordovician and Devonian depositional ages, and transitional to anoxic setting during the Silurian, which can represent the water column progressive stratification stages from Cambrian to Silurian (represented by euxinic sedimentation; Piçarra, 2000; Laranjeira *et al*., 2019) and a mixing stage during Devonian, which is in accordance to these different tectonic environments. Nonetheless, a thorough study is needed, regarding major element geochemistry, and correlation with other metasedimentary formations not included in this work, namely in the Spanish sectors of OMZ and other Variscan (peri-Gondwana) zones, as well as a comparison with Iberian Carboniferous syn-tectonic units, in order to perceive the Variscan evolution trend.

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