Palaeozoic Magmatism Associated with Gold-Antimony-Tin-Tungsten-Lead-Zinc and Silver Mineralization in the Neighbouring of Porto, Northern Portugal

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Abstract. In the studied area there are evidences of Palaeozoic magmatism along the stratigraphic succession from Cambrian to Carboniferous. Igneous, volcanic and sub-volcanic rocks occur along and around a significant Variscan structure, the Valongo Anticline, an asymmetrical antiform anticline, trending NW-SE, located in Central Iberian Zone in the neighbourhood of Porto (Northern Portugal). Mineralizations of gold-antimony-tin-tungsten-lead-zinc and silver occur in the area. Magmatism related to acid and basic subvolcanic and volcanic rocks occurs interbedded in Montalto Formation metasediments (conglomerates, quartzite, wakes and slates) of Cambrian age. In the transition Cambrian-Ordovician (Tremadocian?) underlying the Lower Ordovician massive quartzite of Santa Justa Formation (Floian age), volcanic rocks show bimodal composition and occur interbedded in a lithologic association mainly composed of conglomerate and quartzite with minor slate and wacke intercalations. The acid volcanism consists of interbedded volcanoclastic rocks of rhyolitic affinities and black and green cherts in thick layers represent the basic volcanism. To the top of this basal Early Ordovician volcano-sedimentary succession, overlaying Floian massive quartzites, a succession of interbedded quartzite’s, wackes and slates, enriched in ironstones in the normal limb, and bearing prints of volcanic origin occur. Sub-concordant quartz veins (exhalative-origin) interbedded in the ironstones were interpreted as volcanic layers recrystallized during the circulation of hydrothermal mineralizing fluids. The presence of igneous rocks in Palaeozoic Carboniferous metasediments around Porto is known since middle of nineteen century. Granodioritic porphyry intrusion occurs interbedded in carboniferous metasediments. Metasedimentary country rocks are surrounded by pre- to post-orogenic Variscan granites with no direct spatial relationship with mineralization but hidden granitic apexes suggest an indirect genetic relationship with Sb-Au veins. Chemical analyses were performed on some of the rocks evidencing their origin. Some of them are related to mineralizations. Earlier the main Variscan Au-Sb metallogenic hydrothermal event, metallic preconcentrations (Au, Sb, Pb) occurred during the Palaeozoic, often related to magmatic events.

1. Introduction
Igneous, volcanic and sub-volcanic rocks occur along and around a significant Variscan structure, the Valongo Anticline, an asymmetrical antiform anticline, trending NW-SE, located in Central Iberian Zone in the neighbourhood of Porto (Northern Portugal).
Another prominent structural feature in the studied area is the sinistral "Douro Shear Zone" (DSZ), along the southwestern limb of the Valongo Anticline. Carboniferous basins are settled up all along this structure. Several shear-zones sub-parallel to the DSZ crosscut the studied area, mainly the "Santa Justa Shear-Zone" along the fold axis of the Valongo Anticline (Figure 1).

Mineralizations of gold-antimony-tin-tungsten-lead-zinc and silver occur in the area. Four type of mineralizations were distinguished in the Dúrico-Beirão mining district: Sb-Au, Au-As, Pb-Zn-(Ag) and W-Sn [1].

Mineralizations are generally spatially associated and sometimes genetically to magmatism. The existence of enhanced metal concentrations in Palaeozoic country rocks was evidenced by a geochemical study performed on half a hundred samples, likely sources of metals [1]. Twelve trace elements were analysed: gold, antimony, silver, arsenic, bismuth, cobalt, chromium, copper, nickel, lead, wolfram and zinc indicating the existence of gold and/or antimony and less often lead preconcentrations in some layers, namely in the Cambrian succession (Montalto Formation) where volcanic rocks were identified and in the volcano-sedimentary succession of Lower Ordovician (Santa Justa Formation). The close relation between Sb-veins and Carboniferous basins, recognized since a long time [2], [3], [4], may be explained by the repeated tectonic activity of this major regional structure at various times. Subvolcanic rocks are found in Carboniferous successions in Armorican Massif [5] and in Carboniferous to Early Permian successions in Massif Central [6]. In the studied area porphyries have been found in the Carboniferous succession [7], [8].

2. Geological setting
In the studied area, two principal episodes of folding, one ante-Stephanian and the other one post-Stephanian were recognized [1]. The major ante-Stephanian structure is the Valongo Anticline, N 150-160° E trending with axial plunge toward NW. The anticline is asymmetrical, with a gently dipping (about 40°) northeastern limb and a sub-vertical to slightly overturned southwestern limb [9]. The lithostratigraphic succession of the Valongo Anticline is composed by metasediments with ages between Cambrian and Devonian. Carboniferous metasediments occur west of inverse limb. Along this succession several magmatic rocks have been identified namely subvolcanic and volcanic rocks. Outcropping Variscan granites, surrounding the gold-antimoniferous deposits, are in close relation with Sn-W veins (Figure 1). Hidden granites occurring under the Anticline were also identified, and data suggest a relationship between the Sb-Au veins and these hidden granites [1], [10].

3. Palaeozoic magmatism
In the studied area there are evidences of Palaeozoic magmatism along the stratigraphic succession from Cambrian to Carboniferous, particularly from Cambrian to Lower Ordovician and in Carboniferous. Besides granites, subvolcanic and volcanic rocks occur.

3.1. Granites
No direct spatial relationship of mineralization with outcropping pre- to post-orogenic Variscan granites was found. The hypothesis of an indirect genetic relationship of Sb-Au and Au-As veins with hidden granitic apex is supported by mineralogical data and by the occurrence of altered acid igneous sills in the Sb-Au Ribeiro da Serra mine. In cathodoluminescence the quartz associated with the albitized granite of Ribeiro da Serra show weak reddish luminescence similar to other Variscan granites [11]. Data suggest granites were a trigger for hydrothermal activity or eventually a magmatic source for fluids, metals, and sulphur [10].

3.2. Subvolcanic, volcanic and volcano-sedimentary rocks – stratigraphy and petrography
In the studied area there are evidences of volcanism since Cambrian to Lower Ordovician. Palaeozoic magmatism and in particular volcanic and volcano-sedimentary layers are present along Valongo Anticline from North Valongo to south Arouca.
Figure 1. Geological setting of the study area showing the locations of studied sites. I- Quaternary; II- Carboniferous; III- Ordovician to Devonian; IV- Cambrian; V- syn- to late- F3 granitoids; VI- late-to post- F3 synorogenic biotite granitoids; VII - post-Stephanian granite; VIII- shear-zone; IX - fault; Sites: 1 – Santa Justa; 2 – S. Pedro da Cova; 3 – Fragas do Diabo; 4 – Montalto; 5 – Tapada da Escusa: 6 – Tapada; 7 – Ribeiro da Serra/Alto do Sobrido; 8 – Banjas; 9 – Terramonte; 10 - Gralheira d’Água: 11 – Fragas da Torre; b. Lithostratigraphic Palaeozoic succession in the studied area. 1- slates, arenites, conglomerates, breccias, coal; 2– diamictites; 3- slates; 4- quartzites; 5- conglomerates; 6- rhyolite; 7- basic volcanics; 8- acid volcanics (modified after Couto [1]).

3.2.1. Cambrian magmatism

In Cambrian two Formations were distinguished [1]. Montalto Formation overlaps Terramonte Formation.

The Terramonte Formation is a thick flyschoid succession, with interbedded slates and quartzite, bearing epiclastites.

The Montalto Formation consists of interbedded quartzite’s, conglomerates, pelites, greywackes and volcanic rocks reflecting repeated episodes of volcanism. Altered volcanic acid rocks and exhalites are interbedded in the succession [1]. Green and violet rocks spotted by small yellowish to brownish balls (Fe- and Ti-Fe-oxides), with a matrix of sericite and minor carbonate and lenticular layers of small angular quartz crystals underlining stratification resulted from the recrystallization of a partly vitreous acid volcanic primary rock. Brownish patches and balls differ from the matrix by the abundance of Fe- and (Ti-Fe)-oxides [1](Figure 2a). Dark green laminated rocks, with quartzic layers interbedded with millimetric to centimetre layers of chlorite (Mg-ripidolite), abundant ilmenite, mica (paragonite and scarce pyrophyllite), angular quartz crystals, sericite flakes and carbonates resulting from feldspar
alteration, are interpreted as exhalites [1]. Ilmenite is abundant associated to chlorite (not detrital). No heavy minerals were observed (Figure 2b).

Figure 2. Photomicrograph of volcanic rocks in Cambrian succession of Montalto Formation (around Montalto Mine) (a) Altered acid volcanic rock with abundant sericite and carbonates, resulting from plagioclase alteration and iron oxides (transmitted light, crossed nichols). (b) Exhalite with epidolite in vanes, rhyolitic quartz, sericite in balls (resulting from feldspar alteration) and ilmenite (transmitted light, parallel nichols).

Diabases (altered dolerites) sills occur, interstratified or more scarcely cutting the stratification, mainly in the Cambrian west of the inverse limb but also in the core of the Valongo Anticline. Montalto, Tapada, Ribeiro da Serra and Alto do Sobrido Sb-Au mines and Tapada da Escusa Au-As mine are located in areas where these sills are abundant and thick. These rocks are composed of chlorite (rarely penine), feldspar crystals almost completely altered in sericite, quartz and accessory rutile. Opaque minerals are frequent. Among these, there is a very abundant primary ilmenite (largely altered in leucoxena), a typical signature of the tholeiitic magma and a late generation of quartz. The electron microprobe study of the sample 52M showed that the chlorite has a medium Fe / Mg ratio and punctually high contents of TiO2, probably resulting from the degradation of biotite [1].

Figure 3. Photomicrograph of diabases in Cambrian succession of Montalto Formation with chlorite, feldspar crystals in different phases of altering in sericite, quartz and opaques. (a) Sample from Montalto area (transmitted light, parallel nichols); (b) Sample from Tapada da Escusa (transmitted light, parallel nichols).

3.2.2. Lower Ordovician Volcanism

In the transition Cambrian-Ordovician, underlying the Lower Ordovician (Floian) massive quartzite an Early Ordovician volcano-sedimentary succession (Tremadocian?) occur, in a lithologic succession
mainly composed of quartzite with minor slate and wake intercalations and locally with conglomerate [12]. The volcanic rocks exhibit a bimodal composition (black and green cherts and rhyolitic rocks that are usually interlayered in metasediments but more rarely cross-cut them).

The acid volcanism consists of interbedded volcanoclastic rocks of rhyolitic affinities (Figure 4). Rhyolitic rocks exhibit quartz and alkali feldspar phenocrysts in a fine-grained groundmass. Often volcanoclastic rocks are silicified by hydrothermal fluids. Quartz phenocrysts are commonly embayed exhibiting angular fragments, rounded forms, corrosion gulfs and skeletal morphologies evidenced by cathodoluminescence, with luminescence colours ranging between pink and beige (e.g. at Santa Justa, Fragas do Diabo and Fragas da Torre).

Black and green cherts in thick layers mainly composed of sericite, opaque minerals and abundant recrystallized tourmaline represent the basic volcanism (Figure 5).

**Figure 4.** Rhyolite in the transition Cambrian-Ordovician, Fragas da Torre, Arouca (a) Field photograph of a rhyolite showing a regular orientation of feldspar phenocrysts. (b) Phenocrysts of feldspar and embayed quartz in a fine-grained matrix (photomicrograph, thin section, transmitted light, parallel nichols).

**Figure 5.** Early Ordovician volcano-sedimentary succession (Tremadocian?), Santa Justa. Black chert in thick layers mainly composed of sericite, opaque minerals and abundant recrystallized tourmaline represent the basic volcanism. (a) Field photograph of black chert. (b) Sericite in balls (resulting from pseudomorphosis of feldspar crystals) and recrystallized tourmaline (photomicrograph, thin section, transmitted light, parallel nichols).

To the top of this basal Early Ordovician volcano-sedimentary succession of probably Tremadocian age and overlaying the massive quartzites of Santa Justa Formation (Floian age), a succession of interbedded quartzites, wakes, slates and volcanoclastic rocks occur. In inverse limb of Valongo...
Anticline rocks evidence compositional changes, with sedimentary layers (rounded quartz and abundant heavy minerals) and volcano-sedimentary layers (angular quartz and small sericite skeins resulting from the pseudomorphosis of feldspar crystals, chlorite skeins resulting from metamorphic alteration of Fe and Mn rich sediments, detrital mica in long baguettes and metamorphic muscovite (epizone). In normal limb of Valongo Anticline this volcano-sedimentary succession is thicker containing several layers of ironstones of syn-sedimentary volcanic exhalative origin (seven iron layers were identified) (Banjas mine) [1]. Sub-concordant quartz veins (exhalative-origin) interbedded in ironstones were interpreted as volcanic layers recrystallized during the circulation of hydrothermal mineralizing fluids [1] (Figure 6).

Ironstones exhibit an ignimbritic texture with rhyolitic quartz grains in a chlorite or sideritic matrix, occasionally oolitic. They mainly consist of iron rich chlorite (chamosite) and/or iron rich carbonate (siderite), muscovite, quartz, kaolinite, zircon, tourmaline, rutile, phosphates (apatite), sulphides (pyrite and arsenopyrite dominant), iron oxides and organic matter [1]. In cathodoluminescence volcanic quartz associated to ironstones evidence a flaky texture with luminescence colours ranging between pink and beige similar to the volcanic quartz of the Early Ordovician volcano-sedimentary succession [11].

Figure 6. a) Field photograph of the Floian succession interbedded by volcano-sedimentary layers overlain by Floian massive quartzite (inverted succession) (Alto do Sobrido) b) Floian succession with quartzitic layers showing volcanogenic prints: angular quartz crystals, and flakes of sericite resulting from feldspar alteration (photomicrograph, crossed nichols) (sample 105AS, Alto do Sobrido).

3.2.3. Carboniferous magmatism

The presence of igneous rocks in Palaeozoic Carboniferous metasediments around Porto is known since middle of nineteen century [7], [8]. In present work a granodioritic porphyry was found interbedded in Carboniferous metasediments, near the overthrust of Lower Palaeozoic (Silurian-Devonian) on the Upper Palaeozoic (Carboniferous). The rock evidences a porphyritic texture with angular crystal of quartz, feldspar partly altered in sericite, muscovite, zircon, tourmaline, titanite in a sericitic matrix (Figure 7). Fonseca & Thadeu [13] refer a Cu-Ni mineralization associated to these rocks. The presence of silver was detected by SEM.
Figure 7. Porphyry interbedded in Carboniferous metasediments, S. Pedro da Cova (a) Field photograph of porphyry. (b) Phenocrysts of feldspar and embayed quartz in a fine-grained matrix (photomicrograph, thin section, transmitted light, parallel nichols).

4. Analytical methods and results

Seven of these magmatic rocks, including diabases, volcano sedimentary layers, exhalite, altered acid volcanic rock, epiclastites and diabases were analysed for major elements by X-ray fluorescence on pearls in St Etienne School of Mines. Analytical results are presented in Table 1.

The samples were collected nearby some mines: 56VI - Floian volcanosedimentary layers, Vale do Inferno Mine (Sb-Au); 37AS - Floian volcanosedimentary layers, Alto do Sobrido Mine (Sb-Au); 27TM – Epiclastite, Montalto Formation, Terramonte Mine (Pb-Zn-Ag); 45M – Exhalite, Montalto Formation, Montalto Mine (Sb-Au); 49M - altered acid volcanic rock, Montalto Formation, Montalto Mine (Sb-Au); 52MA - Diabases, Montalto Formation, Montalto Mine (Sb-Au); 150AS - Diabases, Montalto Formation Alto do Sobrido Mine (Sb-Au).

Floian volcanosedimentary layers (56VI and 37AS) and epiclastites (27TM) present high to very high loss on ignition percentages, showing a strong weathering (Table 1). Mobile elements, such as Ca and Na, were certainly leached. The contents in K₂O are occasionally high, but Na contents are always very low (potassic feldspar altered in sericite). The high contents in K₂O (particularly in samples 37AS and 27TM) are essentially related to the abundance of muscovite-sericite.

In exhalite (43M) ilmenite is abundant associated to chlorite (not detrital). No heavy minerals were observed. The variations in the Fe/Mg ratio depend in part on the composition of the chlorites. The chlorite of the exhalite, corresponding to sample 45M [1], is very rich in Mg, thus the low Fe / Mg ratio. Si contents (between 50 and 56%) are much lower than those commonly found in the metapelites (SiO₂ approximately between 60 and 65%).

The sample 49M is a wholly altered acid volcanic rock with greenish to violet colour and foliated texture. Sericite and carbonates resulted from the alteration of plagioclases. Quartz crystals are angular and metamorphism muscovite (epizone) was also observed. It is likely a volcanic glass devitrified. Diabases (52MA and 150AS) are also very altered. Observing the results (Table 1), it can be seen that the diabase corresponding to the sample 150AS is more altered than that corresponding to the sample 52MA sample, with a very high loss on ignition percentages (12.5%) (although 52MA is also very altered a loss on ignition percentage higher than 5%), having suffer leaching of alkalis, Ca, Fe and Mg, with concentration of the most stable elements -Al, Ti, P. The high Ti contents are due to the presence of primary ilmenite, largely altered in leucoxena (a characteristic of tholeiitic magmas). The study of chlorites (Couto 1993) also showed that the chlorite of the sample 52M presents punctually high contents in Ti, probably resulting from the degradation of biotite.
Table 1. Chemical composition of diabase, volcano-sedimentary layers and epiclastites, by FX on pearl.

| Sample | 56 VI | 45M | 49M | 52M | 37AS | 150AS | 27TM |
|--------|-------|-----|-----|-----|------|-------|------|
| SiO₂   | 54.26 | 52.71 | 53.09 | 52.28 | 55.52 | 50.35 | 53.75 |
| Al₂O₃  | 11.80 | 16.36 | 17.46 | 15.62 | 26.91 | 20.51 | 23.03 |
| Fe₂O₃  | 18.11 | 11.31 | 12.73 | 14.69 | 2.64 | 9.70 | 6.75 |
| MnO    | 0.008 | 0.198 | 0.069 | 0.110 | 0.005 | 0.083 | 0.033 |
| MgO    | 0.49 | 8.90 | 2.80 | 5.33 | 0.35 | 0.35 | 2.60 |
| CuO    | 0.04 | 0.38 | 0.11 | 0.08 | 0.03 | 0.09 | 0.04 |
| Na₂O   | 0.16 | 0.43 | 0.18 | 0.06 | 0.37 | 0.04 | 0.67 |
| K₂O    | 2.19 | 0.53 | 0.24 | 1.23 | 7.12 | 0.06 | 5.51 |
| TiO₂   | 0.621 | 2.123 | 1.075 | 3.471 | 1.438 | 4.580 | 0.808 |
| P₂O₅   | 0.03 | 0.29 | 0.06 | 0.15 | 0.09 | 0.76 | 0.12 |
| PR     | 11.30 | 6.78 | 11.24 | 5.76 | 4.67 | 12.50 | 5.74 |
| Total  | 99.01 | 100.95 | 99.08 | 99.60 | 99.14 | 99.97 | 99.02 |

Volcanic rocks interbedded in the Lower Ordovician succession (Sta. Justa Fm): 56 VI and 37AS; volcanic rocks interbedded in the Cambrian succession (Montalto Fm): 45 M - exhalite; 49 M - acid altered volcanic rock; 52 MA and 150 AS - diabases; volcanic rocks interbedded in the Cambrian succession (Terramonte Fm): 27TM-epiclastites

Analysed samples, evidence weak content in SiO₂ (50 a 55%), relatively high contents in MgO - 45M, 49M, 52Ma, and 27TM (<2,5%), relatively high contents in K₂O – 37AS e 27TM, relatively high contents in Al₂O₃ – 45M, 49M, 52Ma, 37AS, 150AS, 27TM. Na₂O and CaO contents are always weak.

5. Discussion
These data are similar to those obtained by Nmila [6] in a study of Permian volcanic rocks of Lodève Basin, Massif Central (France). Enrichment in Al₂O₃ and in K₂O counterbalanced by the impoverishment in SiO₂ and Na₂O occurs in rocks that contain a large proportion of volcanic glass.

Related to the devitrification of volcanic glasses in shallow environment leading to significant use and expulsion of surplus of SiO₂ and Na₂O in the circulating waters. The high contents of Fe₂O₃ are related with the abundance of iron oxides. These data are also comparable to the values obtained for sandstones of active continental margins resulting from a source strongly influenced by acid volcanism [14].

Sagon [15] in a petrographic and geochemical study of about Dinantian volcanism of Bassin de Châteaulin in Britain described different volcanic rocks, namely diabases, rhyolites, that are very similar in texture and composition to those studied around Porto.

As it happens with magmatism, Sb-Au mineralizations are spread along Valongo Anticline, and related to shear zones associated to this structure. There is a spatial association between mineralizations and magmatism. In the area numerous Sb-Au veins occur in these volcano-sedimentary successions. According Couto et al. [4], part of the mineralizations may be even related to magmatic fluids. Cambrian weathered acid volcanic rocks and exhalites (Montalto Formation), Lower Ordovician (Floian) volcano-sedimentary succession, glaciated rocks of Upper Ordovician (Hirnantian) and Carboniferous breccia seems also be related to syngenetic mineralizations (Au, As, Sb and Pb) [1] [4]. Guigues et al. [16] referring to the Portuguese deposits, consider acid volcanism or "spilitico-keratófiro" (bimodal acid-base) a guide for the prospecting of antimony. The remobilization of antimony, from the Cambro-Lower
Ordovician rhyolites, was defended by some authors for the deposits of the Central Massif and of the Armorican Massif. Picot et al. [17] proposed a volcanic origin for the antimony and gold deposits of the Armorican massif and possibly of the Central Massif. According to the same authors, Brioverian gold is connected to the basic volcanism being the antimony in the Cambrian, related to the acid volcanism. Gumiel & Arribas [18] considered that, in the Iberian Peninsula (Central-Iberian Zone) volcanism was mainly responsible for the antimony and mercury mineralizations. According to these authors, from the Lower Palaeozoic to the Lower Carboniferous [18], there were several stages of pre-Variscan volcanism, giving rise to antimony exhalation deposits. The hypothesis of remobilization of antimony from Cambro-Tremadocian rhyolites was suggested by some authors for the deposits of the Central Massif and of the Armorican Massif (France) [19] [17]. After Guillou [20], sedimentary antimony mineralizations of the Lower Palaeozoic carbonate of the Asturian Geosinclinal are associated with a rhyolitic and albitofiric volcanism.

6. Conclusions

It is noted that the magmatic analysed rocks have a very different composition from the metasediments. They are poor in Si, with iron-magnesium affinity. The strong variations of certain elements (Fe, Mg, Al...) show that the chemistry of the deposition environment was very variable. The unusually low contents of Na and Ca may be explained by a leaching caused by a strong meteoric weathering, which affected all the samples. However, the contents in K are sometimes high and potassium has been less leached than Na. In the studied area Palaeozoic magmatism expressed by dolerites, rhyolites, porphyries, among others, evidence a continuous spreading from Cambrian to Lower Ordovician. This fact implies the existence and proximity of an important volcanic activity expressed throughout the sedimentation, in great part related with the rifting of the Rheic Ocean. The magmatism is again recorded in the Upper Carboniferous in relation with magmatic episodes occurring in the end of this period, maybe related to the uplift of Variscan belt [21]. This magmatic input, synchronous with the sedimentation, may have contributed to the concentration of metals. Previous studies showed the existence of enhanced concentrations of metals (gold, antimony, lead) in some rock layers, mainly in the Cambrian and Lower Ordovician (Floian) volcano-sedimentary successions bearing ironstones [1] [4].

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