W-molybdenite in Silurian meta-volcanic rocks of Northern Portugal

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In Silurian metavolcanic formations of Serro (Serra de Arga, Minho, Portugal), proto-volcanogenic felsic rocks have high contents of disseminated sulphides.

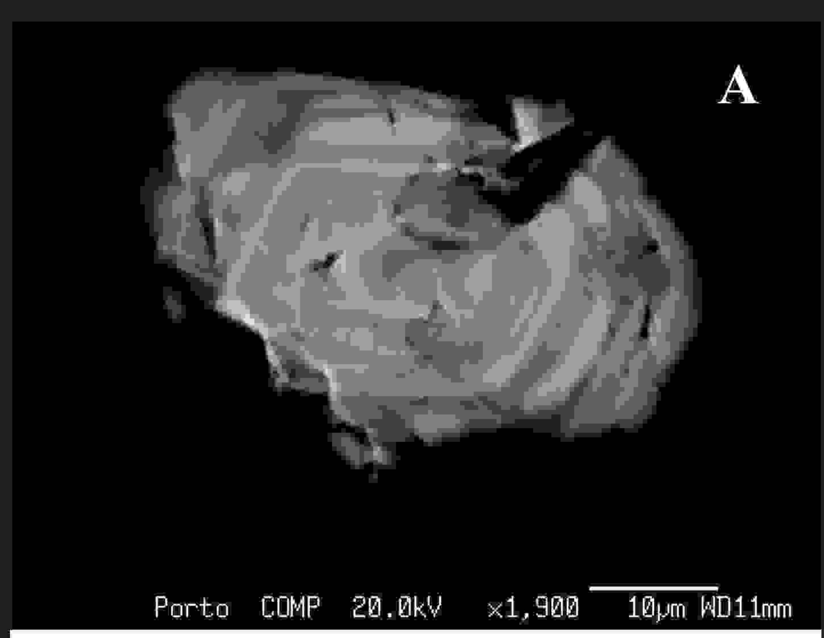
Detailed petrographic analysis, on macroscopic and microscopic scale, of samples from outcrops and boreholes (archive form LNEG), allowed a fine textural description of the facies and the characterization of the related mineralization.

Through electronic microprobe analysis, it was possible to detect and refer on protovolcanics an essentially rare mineralization - W-molybdenite.

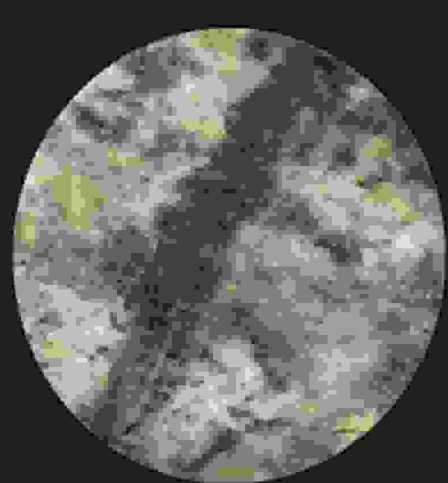
The W-molybdenite is considered an exceptionally rare phase (among the various occurrences of W and Mo minerals, molybdenite and scheelite are the most stable ones), formed in association to metasomatic processes. Mo is actually quite susceptible to fluid mobilization and concentration.

In the bibliography which can be found on the subject are few references to the solid solution tungstenite-molybdenite, which is experted because of the host crystal structures are similar.

Moh, G & Udubasa,(1976) showed experimentally the variability between Mo (molybdenite) and W (tungstenite) end members in the solid solution (Mo W) S2; Holl, & Weber-Diefenbach, (1973), observed W-Mo phases as scheelite hosted inclusions in replacement products in Ferbetal paradigmatic deposit (a solid solution was observed); W rich-molybdenite was described by Barkov et al 2000, in fenites of the Kola alkaline Complex - venular and automorphic zoned textures and compositions up to 5.85% W in crystals core.



EPMA - BSDE image of W-molybdenite.



W-molybdenite occurs at Serro, on tuffite -pumice facies that can be traversed by tourmalinite veins with crack-seal (B).

The mineralization has automorphic hexagonal character (A), and occur in small sized crystals (A - EPMA – BSDE image).

Electronic microprobe observation and analyses, allowed the establishment of the more typical compositional zoning. The main constituents were determined in Hyperprobe Jeol JXA-8500F operating at 15KV.

The analyses show however some composite effect, determined by the limited thickness of the areas with homogeneous composition;

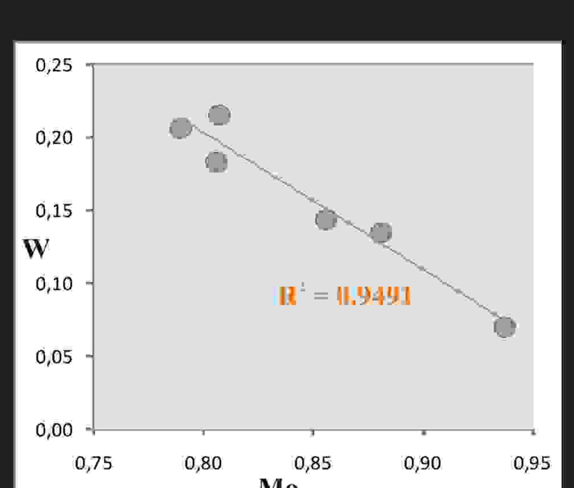
Figure A suggests the oscillatory behaviour of compositional evolution, and a consistent general compositional trend from core to rim - border enriched in Mo. W occurs in significant amount in crystals core (maximum determined content of W = 20,28%) - C.

Once calculated the structural formulas of the different compositional populations, there is the following variation (Fe[illegible] Mo[illegible] W[illegible])S2.

C

	Wt% Fe	Mo	S	Se	W	Total	% atoms (apfu) Fe	Mo	S	Se	W
1	0,1755	46,51	34,87	0,027	13,59	95,17	0,01	0,88	1,98	0,00	0,13
2	0,0738	49,61	35,18	_	7,16	92,02	0,00	0,94	1,99	0,00	0,07
3	0,1664	46,11	35,89	_	14,79	96,96	0,01	0,86	1,99	0,00	0,14
4	0,1083	41,65	34,64	0,0083	18,06	94,47	0,00	0,81	2,01	0,00	0,18
5	0,1809	40,58	34,3	_	20,21	95,27	0,01	0,79	2,00	0,00	0,21
6	0,1591	39,8	32,46	0,0105	20,28	92,71	0,01	0,81	1,97	0,00	0,21

Results of point chemical analysis (electronic microprobe) of W-molybdenite phase.



Correlated variation of W and Mo. Trend established for apfu.

From the diagram D, is noted a negative correlation between W atomic contents variation and Mo relative increase. Homovalent replacement W-Mo is suggested by the definition of projections along the line of reference (W, Mo)=1 with R = 0.949.

THE VOLCANOGENIC SUCCESSION

The main volcanogenic facies in the Serro succession are the following:

- Pumice breccias - lenses consisted of quartz and plagioclase intergrowths with flux bands and pumice vesicular clasts that evolved by compression and dissolution for diffuse domains of phyllitic alteration (F). The sulphides are abundant (note the conditioning of sulphide to phyllitic layers). The textures are interpretable as a result of pyroclastic flows. Show great thickness, reflecting the extensive character of the eruption. The predominant sulphide enrichment related to these rocks is due to conditions of permeability which facilitate fluids progression. Contents of elements normally characterized by a lower mobility show compositional match to calcalkaline andesites and arc lavas.

- Polygenic rhyolitic lavas - correspond to siliceous lavas with high crystalline volume (low glass component):
1- Banded microcline rocks - bands with distinct composition of quartz, albite and pink microcline (M). Protolithic hypothesis – coherent banded rhyolite lava, with planar flow bands.
2- Granular quartz-feldspathic rocks with biotite and muscovite, sometimes with quartz phenocrysts. Local transitions to finer-grain granular rocks with the same representative composition was observed, (possibly tabular bodies with sharp contacts) (N). The sulfides are scarce or absent. Protolithic hypothesis - porphyritic rhyolitic lavas and synvolcanic intrusions. The absence of chilled-margin confirms the more or less simultaneous consolidation of the lava and synvolcanic rock. Chemical analysis of the quartz-feldspar lithological therms is consistent with calc-alkaline to transitional compositions.

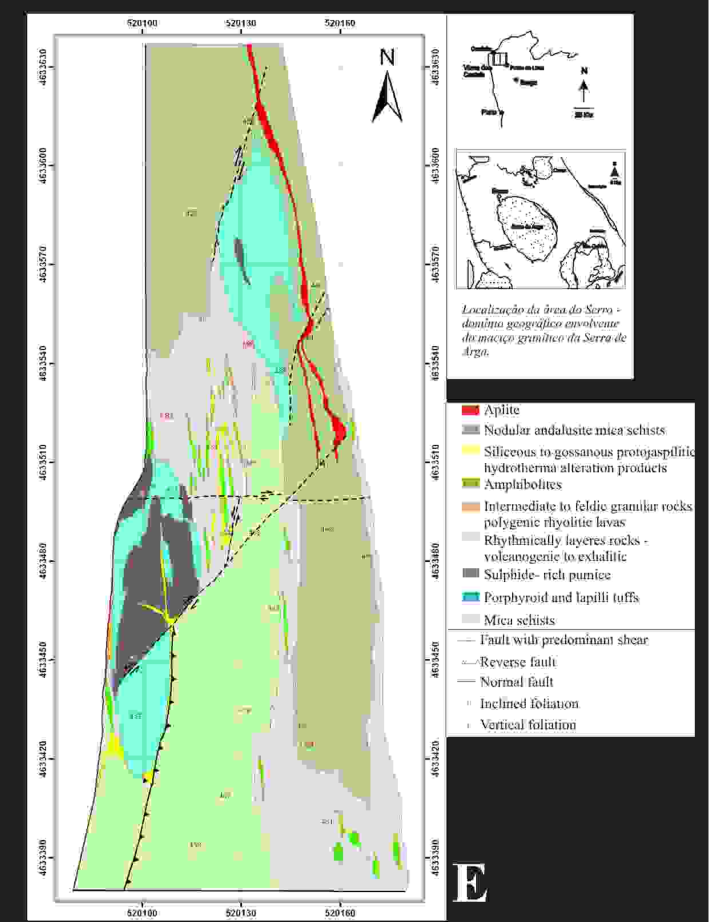
- Porphyroid and lapilli tuffs - Predominantly banded albitic facies, whith quartz and albite phenocrysts, and sometimes lapilli clasts (G,H,I). Generally, pyroclastic fragments are small. The sulphides can be abundant or absent. Alteration of the primary paragenesis originates pseudomorphic argillic-sericitic alteration of plagioclase, chlorite and dravite precipitation. The changes induced by fluids with regional circulation can be correlated to episodes of sulphide remobilization. Protolithic hypothesis - successive accumulation of ash and pyroclastic materials.

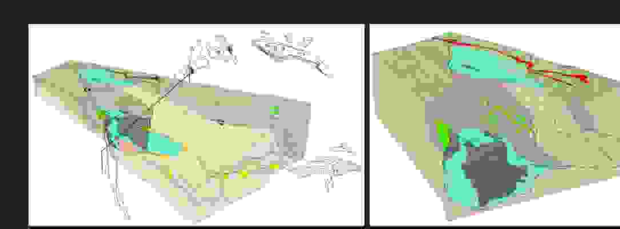
- Exhalative to subexhalative facies - Exahlitic activity succeeds the instalation of porous vulcanoclastic facies. Very permeable conditions associated with the pyroclastics limited however the possibility of exhalites formation.
1-Lenticular oligonite on pumice clast (Q). Protolithic hypothesis – Mn contents remobilization, that are normally connoted to exhalative activity; replacement of porous facies.
2- Jaspilitic gossan, with some goethite and amorphous silica (P). Fe oxides and sulphides are scarce. Protolithic hypothesis – jaspilitic trend facies, formed under exhilative conditions by fluids emanating to the surface.
3- Crack-seal venulation with massive dravite (B). Protolithic hypothesis - at least two episodes of fracturing and precipitation of tourmaline by B-rich fluids.
4- Venular to stratiform tourmalinite. Dravite-pyrite intergrowths (Y). Protolithic hypothesis - tourmalinite formation by exhalative precipitation on the surface, before sulphides deposition; cataclasis and brecciation.

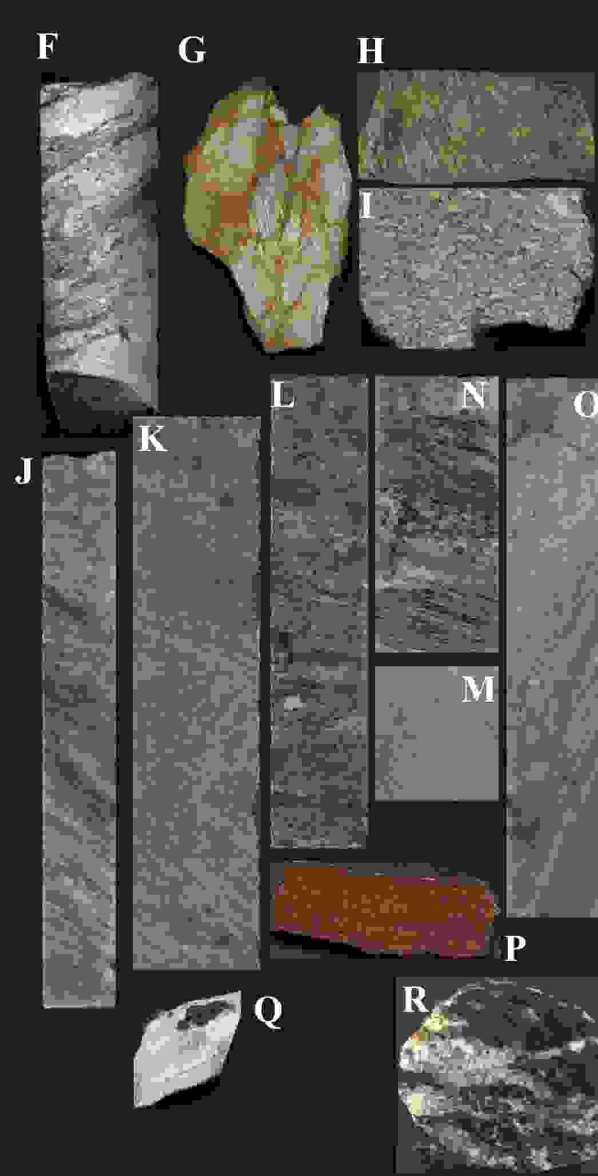
- Amphibolites with relict volcanic textures - quartz-feldspathic rocks with amphibole show porphyritic and clastic texture relics (N).

- Amphibolites with plagioclase felsic segregations (R)- Amphibolites are geochemically equivalent to tholeiitic basalts. Plagioclase segregations are more or less boudinaged and stromatic. Protolithic hypothesis - sinvolcanic maphic intrusions subject to partial melting and leucosome segregation.

- Calcsilicate Rocks - banded to almost monomineralic rocks, with calcsilicated mineralogy (O)- grossularites, epidotites, actinolitites, clinozoisitites and garnet amphibolites interlayered with psammitic facies. Protolithic hypothesis - there is some undetermination regarding its genetic affinity - carbonate sedimentary or pre-metamorphic hydrothermal alteration of tuffite protoliths or subexhalative rocks.







RELATED SULPHIDE MINERALIZATION

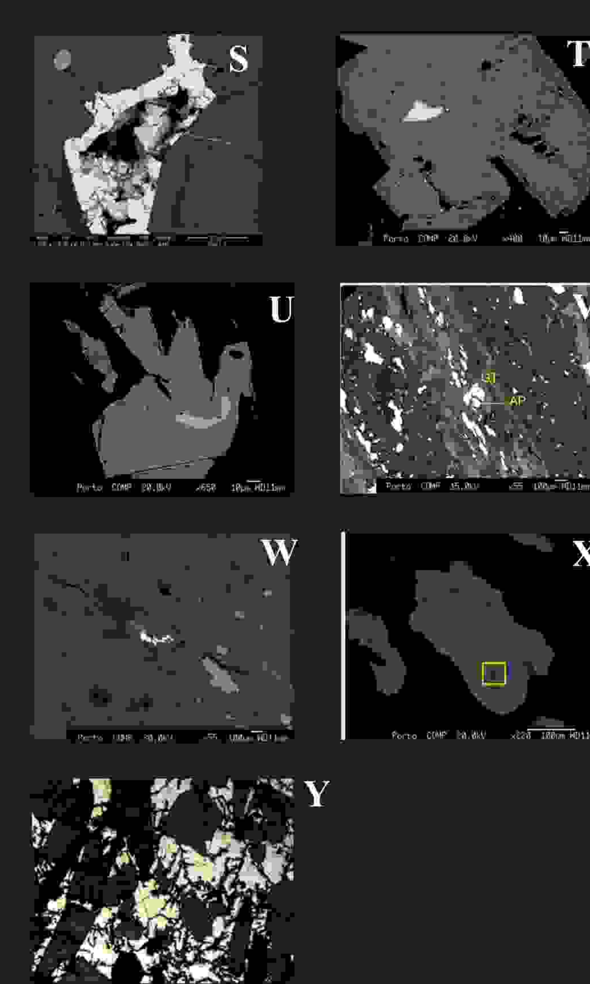
The mineralization is associated with vulcanoclastic rocks (pumice), some tuface facies and amphibolites. Rocks that do not include mineralization (postdate the mineralization or do not manifest conditions of permeability to the progression of fluids) are coherent metarhyolites and some lapilli pyroclastic facies.

- The distribution of Serro mineralization (banded sulphides, disseminations, rare veins, without stockwork) can be interpreted as metasomatic replacement below surface conditions, using physical characteristics of porosity and permeability, characteristic of pumice volcanic facies.

Mineralizations occurring in metavolcanics are represented by pyrite and pyrrhotite associations with compositional homogeneity. The mineralization is affected by remobilization, metamorphic recrystallization, deformation and metamorphism.

- Pyrite and pyrrhotite - pyrrhotite mineralization is most abundant. Automorphyc crystals are the result of metamorphic recrystallization and almost always host sphalerite, galena and arsenopyrite inclusions (T, U) - recrystallization combined with annealing-recovery. Within few crystals of automorphic pyrrhotite, miarolitic cavities are coated by late pyrite (S). Pyrite and pyrrhotite (which results from pyrite inversion in progressive metamorphism) are mostly anhedral and often have inclusions of quartz and phyllosilicates. Correspond to banded disseminations after remobilization and deformation, contemporary to phengite alteration (V). Pyrite also forms fracture deposits (tension gashes with sigmoidal geometry) and was observed precipitated in fractured tourmalinite. Pyrite admits variable percentages of Co-Ni subsitution. Several authors suggest the use of Co / Ni ratio in view to estimate the conditions of formation. In Serro two groups of Co / Ni are observed: values close to 10 and occasionally higher (primary volcanogenic pyrites with up to 23 Co/Ni ratio) and values closer to 1 (remobilized hydrothermal pyrites).

- Sphalerite and galena - show the same paragenetic relations with pyrite suggesting coupled crystallization. Sphalerites and galenas show peculiar geometries in carrier pyrite. The association of sphalerite, galena and arsenopyrite with pyrite inclusion relations - pyrite overgrowth, result from reorganization of primary sulphides in face of metamorphic recrystallization. It was also observed sphalerite without pyrite generation. Galena is associated with pyrite in late microfractures (appears as an extension of pyrite veinlets) (W) and isolated with peripheral molybdenite. Zn/Cd contents in sphalerite have petrogenetic connotation. Overall Cd is high and the obtained Zn / Cd compositions (273.29 - 411.87) are close to volcanogenic facies (high values of the ratio).



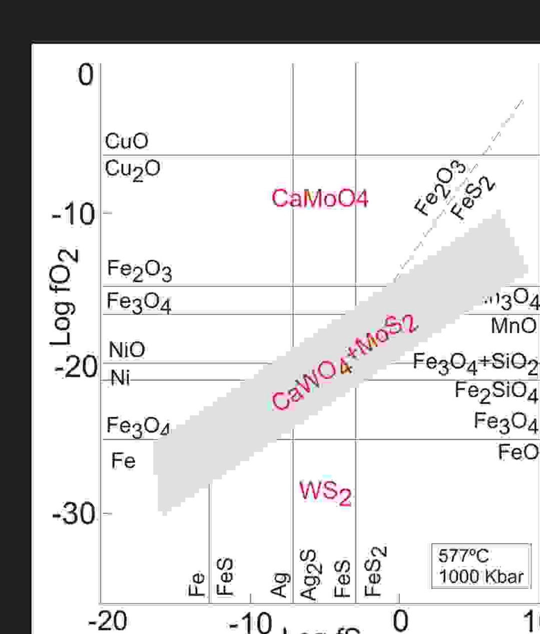
CONCLUSIONS

In Serro, the presence of W-molybdenite in felsic meta-volcanics suggests peculiar conditions to the evolution in a primordial hydrothermal stage. According to the experimental data of Holl & Weber-Diefenbach, 1973 and Hsu, 1977, W enrichment in molybdenite is correlated with high sulfur activity during early crystallization. W is incorporated as W4+.

The factors that govern variability of Mo and W mineralization and the occurrence of replacements in their crystal lattice depend essentially on the mobility / transport, saturation and degree of oxidation. fS2 and fO2 are the parameters that provide needed to move the balance from tungstenite (W4 +) towards the precipitation of molybdenite, scheelite + (W6 +) and after powellite (CaMoO2). Figure Z shows the curves limiting the stability of phases and associations at temperature values equal to 577º C and 1000Kbar (according to Hsu, 1977).

The textural and compositional relationships of the observed crystals - oscillatory zoning, Mo-rich overgrowths and aspects of corrosion - suggest rebalancing with several and repeated fluctuations of oxidation degree (fO2) in the growth medium. According to Hsu (1977) Mo enrichment to the rim is accompanied by increasing fO2. At the same fS2, tungstenite forms at lower fO2 compared to molybdenite (Fig. Z, Hsu, 1977).

The introduction of W in the system possibly accompanied water-interaction, concomitant with the deposition of sulphide mineralization, in a VHMS type model. The evolution to an oxygenated environment would reflect the observed deposition of vein tourmalinites (Cr-rich dravite) in protoliths including W-molybdenite, possibly due to exhalitic mineralization. Also, it would facilitate the occurrence of molybdenite, without W content, which is observed in metafelsites, and scheelite, occurring in calcsilicate rocks and amphibolites of the same suites.



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