Picture by F. Noronha

Santa Helena breccia pipe a new type of W deposit in Iberian W-Sn Metallogenic province (Borralha, N Portugal)

PICO – EGU2018-16190

Gonçalves, A.*, Lima, L., Ramos, V., Noronha, F.

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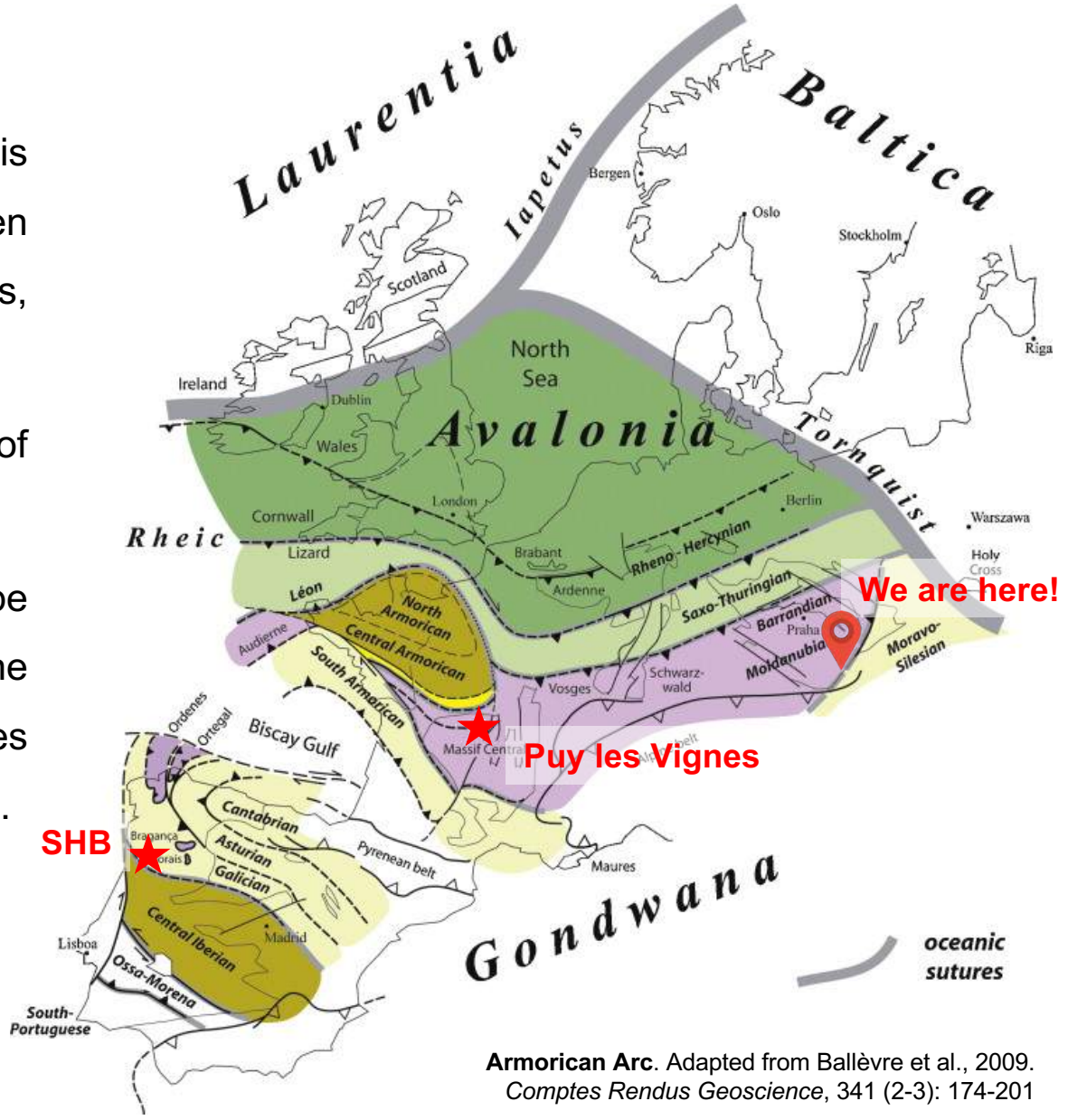
The aim of this work is to give a contribution for a better knowledge of Santa Helena Breccia. The main mineralization is of W, although other oxides (Ti, Sn, Nb, Ta), native Bi and sulphides are also present, being a potential new mine.

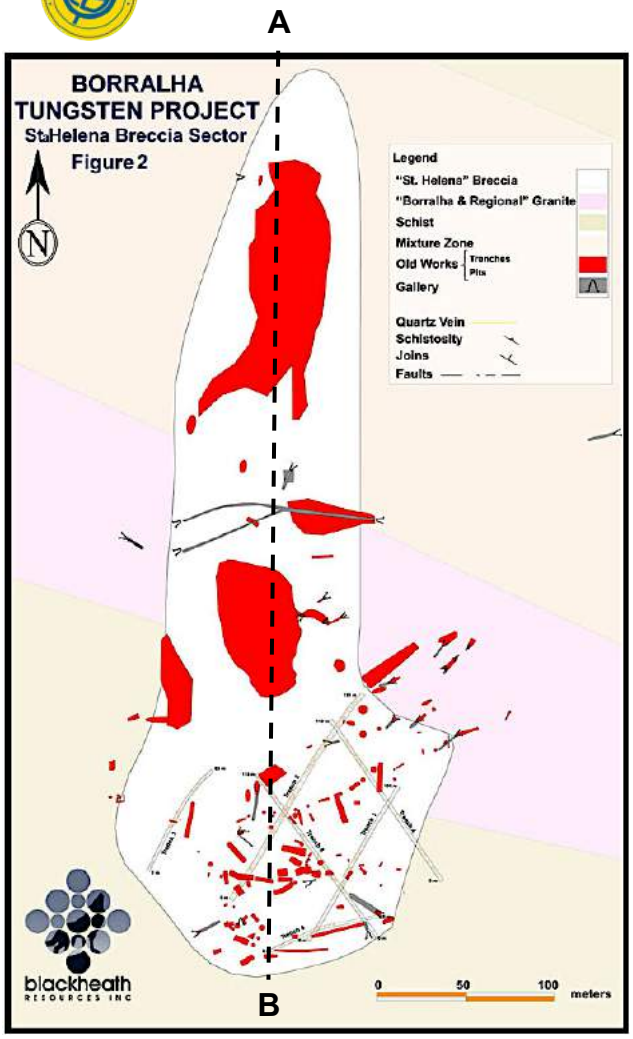
Geological Setting

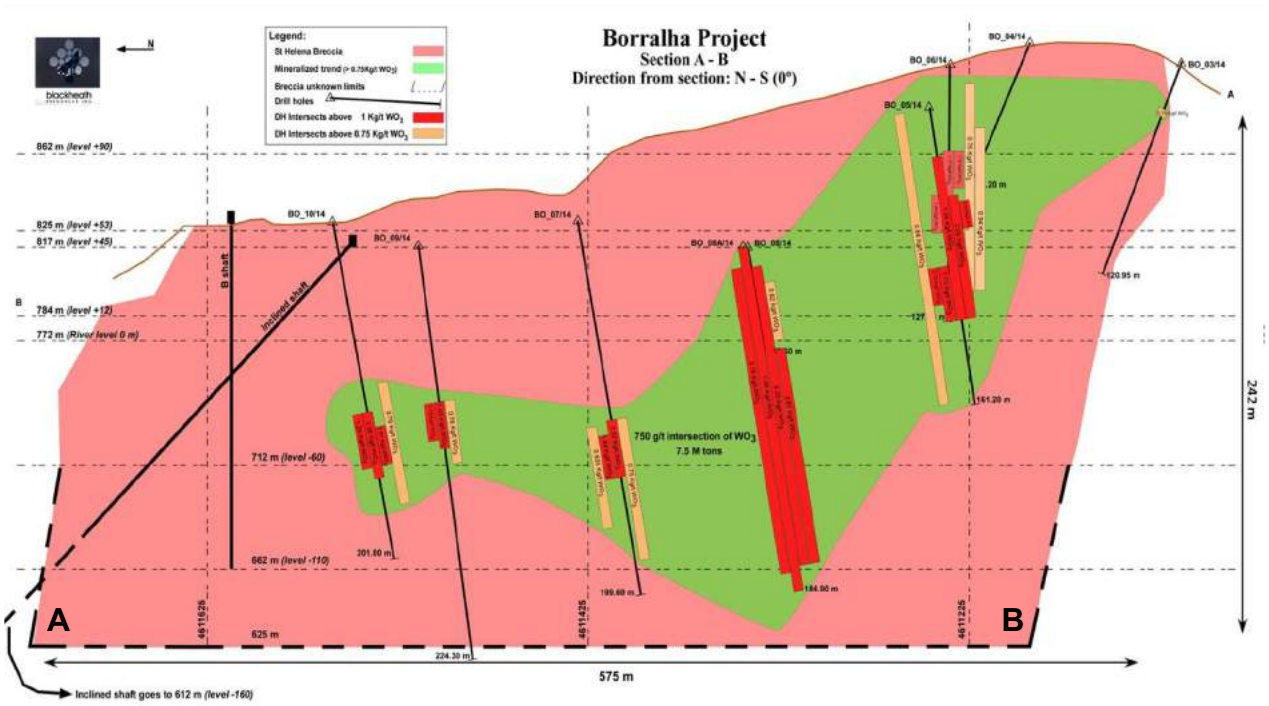
- **S**anta **H**elena **B**reccia (SHB) is located in the contact between Central Iberian and Galician zones, in North of Portugal;
- This is a very **uncommon** type of **W deposit**;
- Only one more example of this type of deposit is described in the **European Variscan Belt -** Puy les Vignes, in Massif Central Français.



Armorican Arc. Adapted from Ballèvre et al., 2009. *Comptes Rendus Geoscience*, 341 (2-3): 174-201

Why is Santa Helena Breccia so special?



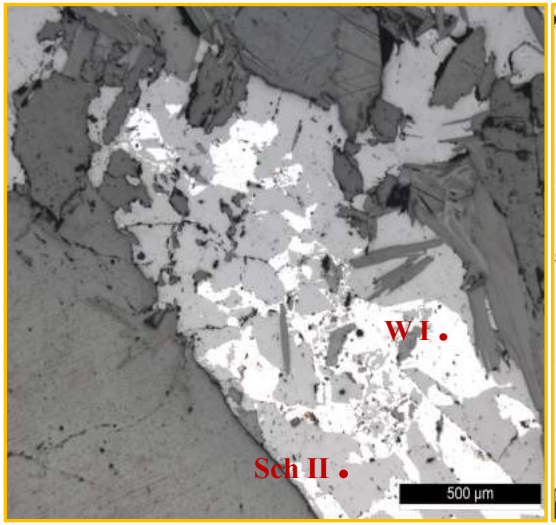


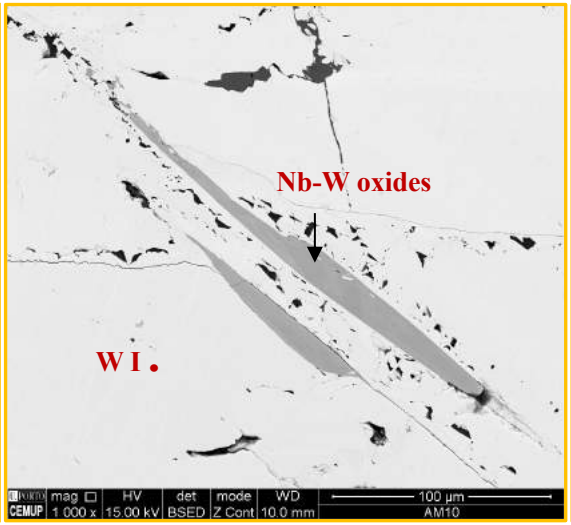
- **Disseminated W mineralization** in the ore body;
- Classified as an collapse breccia cemented by a **mineralized hydrothermal quartz**;
- A mineral association characterized by a **low content of sulphides** and total volume of 40-50 Mt, where **22.5 Mt with a grade average of 750 g/t WO3**;

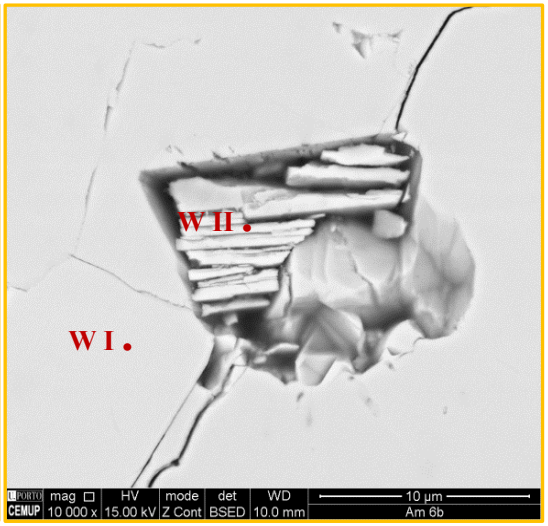
to exploit as an open pit mine

Which are the ores in SHB?

The petrographic observations led to the definition of 4 mineralization stages: **I (Ti, Sn, W, REE), II (W, Nb-Ta)**, III (Fe, Cu, Zn, Mo, Sn) and IV (Bi, Pb-Ag), where the **1st and 2nd stages are the most important**.







Main conclusions

- The presence of **disseminated W mineralization** with **high grades** and the **large volume** of SHB pipe, allows the exploitation as an **open pit mine**.

- The exploitation of a "**Critical Metal**" in a poor region of Northern **Portugal**, with old mining traditions, would be crucial to improve its economic and social development.

Thank you very much for your attention!

See you on:

PICO SPOT 3 – PICO screen PICO3.5

Session GMPV2.9/PS6.3 – Metals and sulphides in magmatic systems: from core formation to ore formation.

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PICO viewing – EGU2018-16190 – *other studies*

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SUBJECTS

Background

Regional geology

Santa Helena Breccia

Other studies

- Distribution of the W contents in depth
- Occurrence of the W mineralogy in the drill cores
- Geochemical characterization of the Santa Helena breccia
- Mineralization stages
  - Stage I (Ti–Sn-W- REE)
  - Stage II (W ± Nb-Ta)
  - Stage III (Fe-Cu-Zn ± Mo ± Sn)
  - Stage IV (Bi ± Pb ± Te-Ag)
- Hydrothermal alteration in hand samples
- Hydrothermal alteration in polish thin-sections
- Distribution and mobility of REE during the hydrothermal alteration

Main Conclusions

References

Publications

Background

- **Borralha mine** (1904-1985) was the 2nd largest W mine in Portugal after Panasqueira, **exploiting vertical and sub-horizontal quartz veins with wolframite and scheelite** associated with sulphides, native bismuth and Pb-Bi-Te-Ag sulphosalts.

- **Borralha deposit** has the particularity to have, in addition of the vein structures, two mineralized breccia pipes: **Santa Helena (SHB)** and Venise.

Fig. 1 Landscape of Borralha Mine (http://www.blackheathresources.com/s/Borralha.asp accessed in 2nd April 2018).

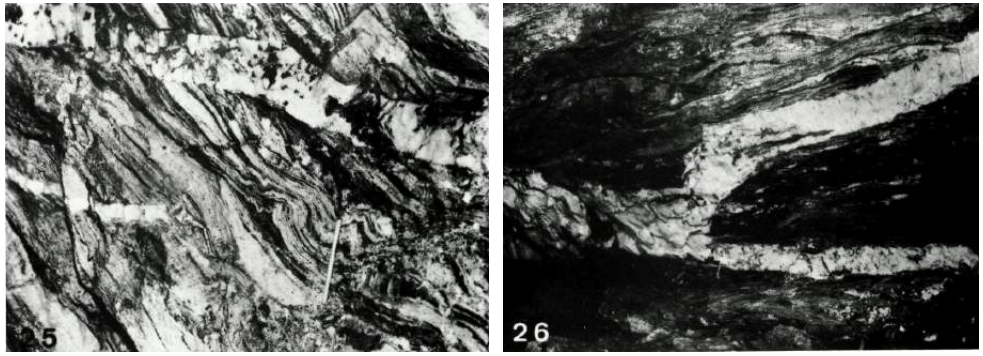

Fig. 2 Sub-horizontal and vertical mineralized hydrothermal quartz veins from Borralha mine (Noronha, 1983). The **total production** of wolframite and scheelite concentrates (65% WO_3), was estimated at about **18,500 t**.

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Regional Geology

- **Borralha area** (Montalegre district, N Portugal) is located at the NW of the Iberian Peninsula in the boundary between Central Iberian and Galician zones.

- **Silurian metamorphic rocks**;
- **Synorogenic granites**: *Syn*-D_3 porphyritic biotite granite (Borralha granite) and two-mica peraluminous granites; *Post*-D_3 leucocratic granite (Penedos granite).

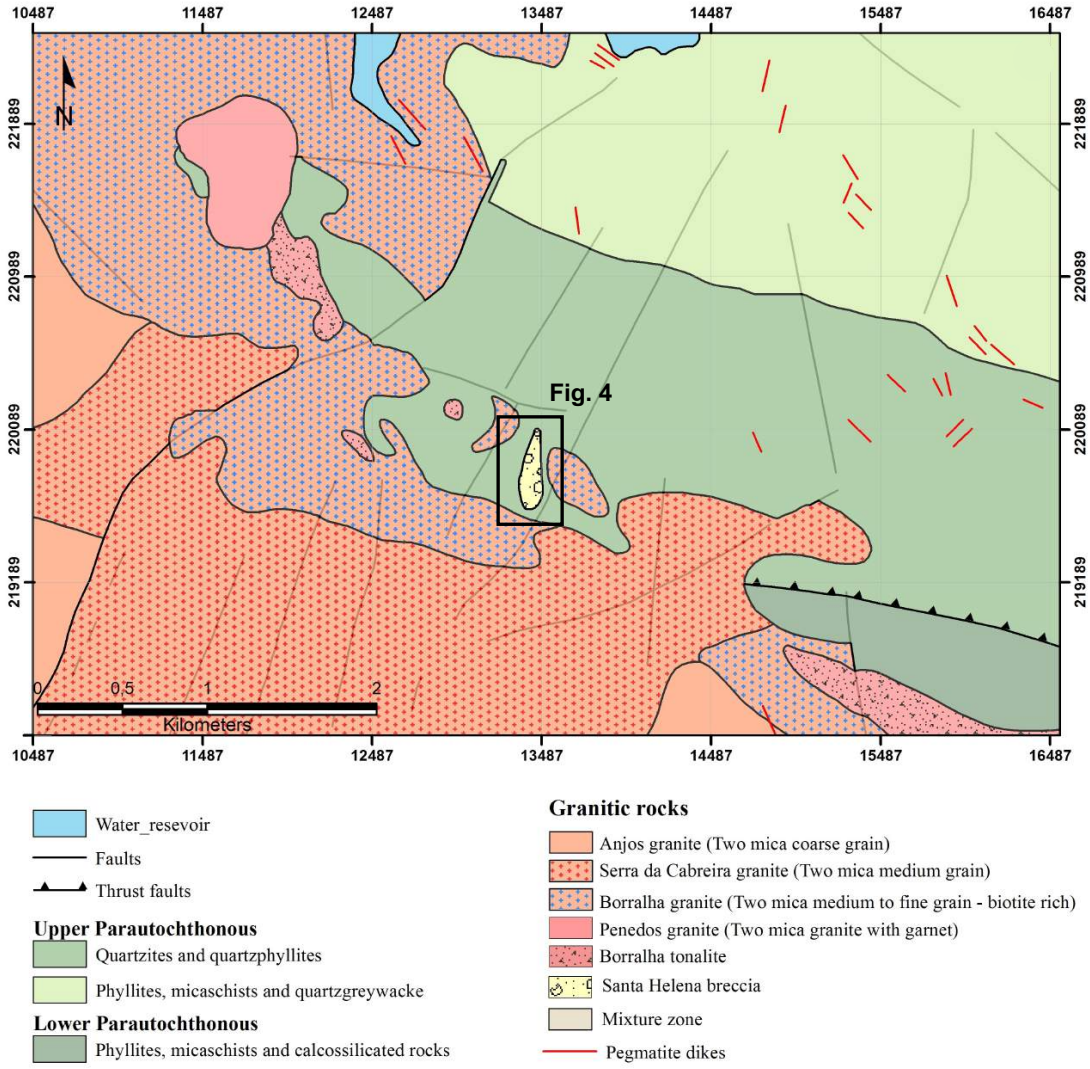

Fig. 3 Simplified geology of Borralha area based on 1/50000 scale geological maps (6A - Montalegre (Noronha & Ribeiro, 1983), 6C - Cabeceiras de Basto (Ribeiro et al., 2001)), using coordinate system ETRS_1989_Portugal_TM06.

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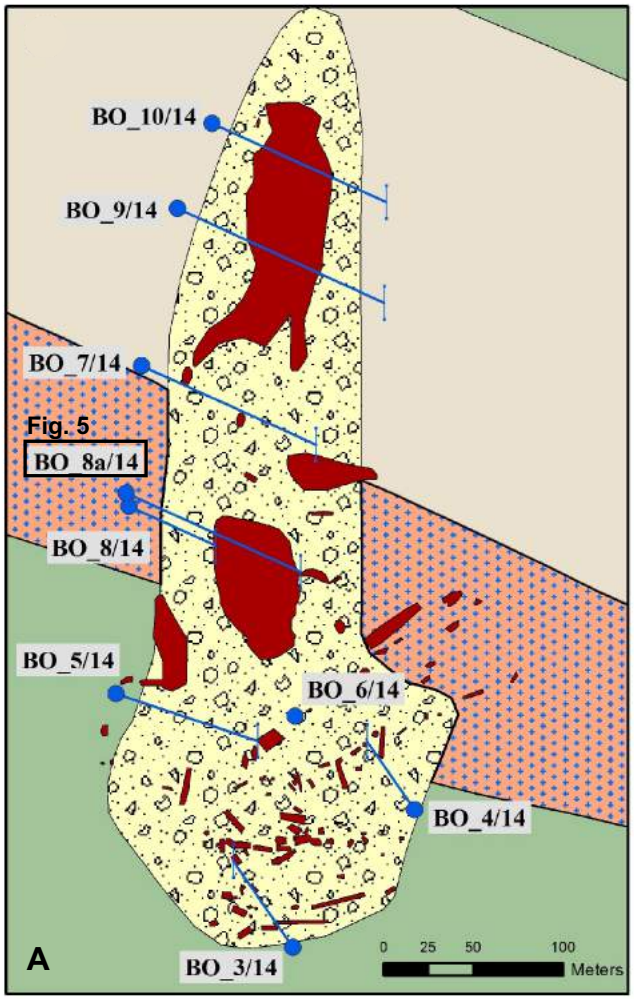
Santa Helena Breccia (SHB)

- Sub-vertical N-S structure cutting the contact between the Borralha granite, metasedimentary rocks and a “mixture zone” (schist ± granite) (Noronha, 1979).
- Ellipsoid shape: 575 m in length, over 150 m in width and over 200 m in depth (it is known in -135 level mining works).



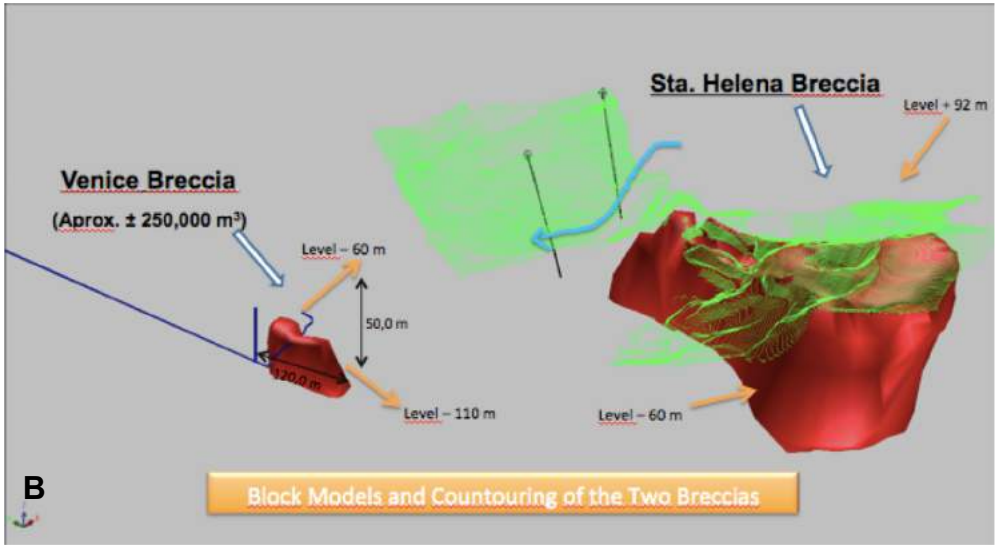


Fig. 4 A. Simplified geology of Santa Helena breccia (blackheath resources, 2nd April 2018). See simbology used in fig. 3. **B. 3D model of SHB located in Borralha W Mine** (model provided by the Consortium Blackheath and Mineralia Lda.)

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Santa Helena Breccia (SHB)

- Fragments are **angular** with **very variable sizes** and with **similar lithological composition of the surrounding regional rocks**, **cemented by hydrothermal mineralized quartz ± micas**.
- A **consistent hydrothermal alteration** is observed, mainly near the **contact cement-fragments and in late fractures**
  - occurrence of **2 generations of muscovite, quartz and 4 generations of chlorite**.
- This breccia was interpreted as a **collapse breccia** (Noronha, 1979).

Fig. 5 Representative sample from Santa Helena breccia collected in BO_8a/14 drill core (cores provided by the consortium Blackheath and Minerália, Lda.).

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Distribution of the W contents in depth

- **Geochemical values** collected in **different lithologies** allowed to analise the **distribution of W contents**;
- The **most significant W contents** (275 to 17600 ppm of W) occur from the **106 to 176 m** corresponding to domains of **breccia with some oxidation, boxworks and medium-grained wolframite** (see: Gonçalves et al., 2017-Com. Geol. extended article).

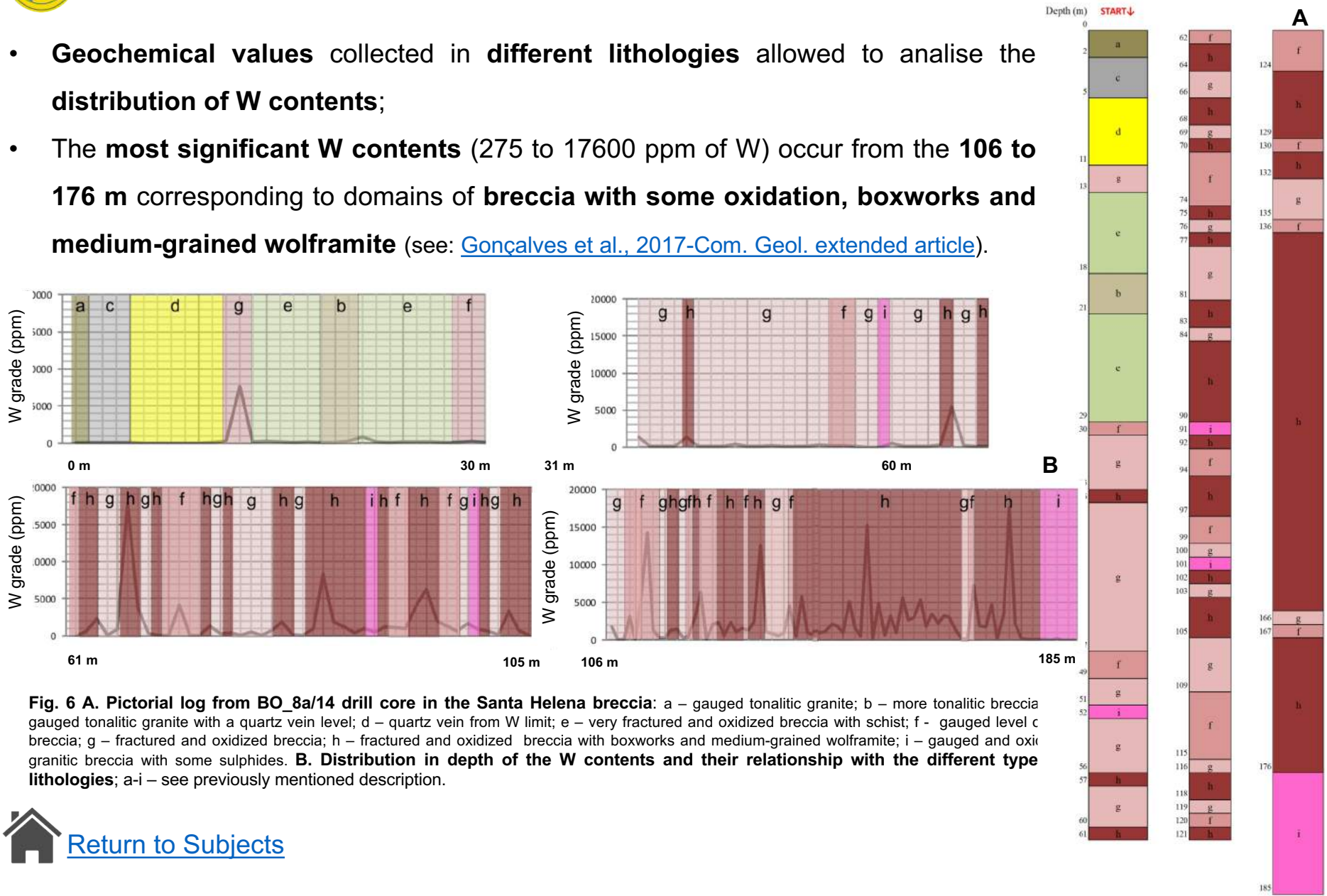

Fig. 6 A. Pictorial log from BO_8a/14 drill core in the Santa Helena breccia: a – gauged tonalitic granite; b – more tonalitic breccia gauged tonalitic granite with a quartz vein level; d – quartz vein from W limit; e – very fractured and oxidized breccia with schist; f - gauged level c breccia; g – fractured and oxidized breccia; h – fractured and oxidized breccia with boxworks and medium-grained wolframite; i – gauged and oxi granitic breccia with some sulphides. **B. Distribution in depth of the W contents and their relationship with the different type lithologies**; a-i – see previously mentioned description.

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Occurrence of the W mineralogy in the drill cores

- Identification of **wolframite and scheelite**, where the first one is more abundant.
- **Different types of disseminated tungstates** were identified:
  - fine to very fine- grained wolframite and scheelite, in the fragments;
  - medium (> 5 to 10 mm) to coarse-grained (> 10 mm) wolframite in the cement;
    - in both cases associated with **muscovite I and II ± quartz ± Fe chlorite** (Bobos and Noronha, 2017);
  - coarse-grained (> 10 mm) wolframite in late hydrothermal quartz veinlets.

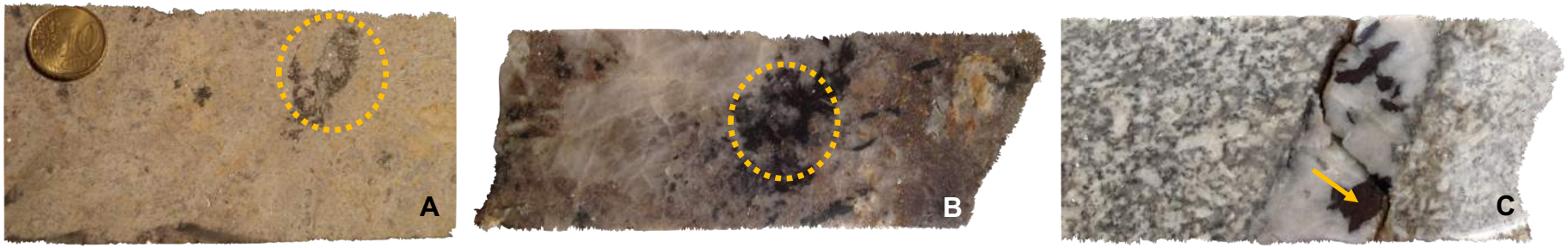

Fig. 7. Types of occurrence of the W mineralization in the Santa Helena breccia. A. Fine to very fine-grained wolframite and scheelite, in the fragments. B. Medium (> 5 to 10 mm) to coarse-grained (> 10 mm) wolframite in the cement. C. Coarse-grained (> 10 mm) wolframite in late quartz veins cutting the breccia.

Return to Subjects

Geochemical characterization of the Santa Helena breccia

Associated with tungsten mineralization (W>200 ppm)	
Altered breccia	Pegmatite and micaschist; hydrothermal alteration represented by small crystals of muscovite (ms); disseminated medium crystals of wolframite (wf) (Fig. A).
Breccia with quartz cement	Micaschist cemented by quartz; hydrothermal alteration represented by small crystals of ms and some chl; medium to coarse-grained wf (Fig. B).
Altered pegmatite	Pegmatite and micaschist; presence of random medium to coarse-grained ms; disseminated medium crystals of wf in the pegmatite fragment (Fig. C).
Altered fragment	Lithology with granitic composition with strong hydrothermal alteration represented by fine to coarse ms and chl. In specific areas, fine-grained wf can be observed (Fig. D).
Leucocratic fragment	Lithology with aplitic texture extremely altered. The alteration is represented by an intense muscovitization giving to the sample a light color (Fig. E). Disseminated wf.
Fine- to medium-grained two mica granite	Apparently unaltered fragment of medium- to fine-grained two mica granite (Fig. 2). Disseminated wf.
Late quartz vein with wolframite	Late quartz vein with clay minerals resulting from alteration of the K-feldspar and some oxides. It is possible to identify random chl. Coarse-grained wf (Fig. G).
Barren lithology (W<200 ppm)	
Medium- to coarse-grained two mica granite	Medium- to coarse-grained two mica granite partially altered (Fig. H).

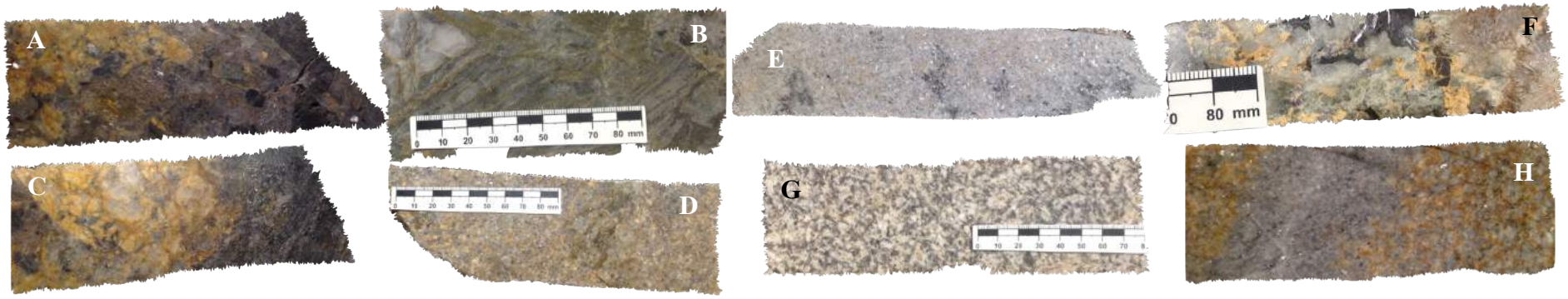

Fig. 8 Representative samples from each lithology that composes de SHB. See Gonçalves et al., 2018 - CNG

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Geochemical characterization of the Santa Helena breccia

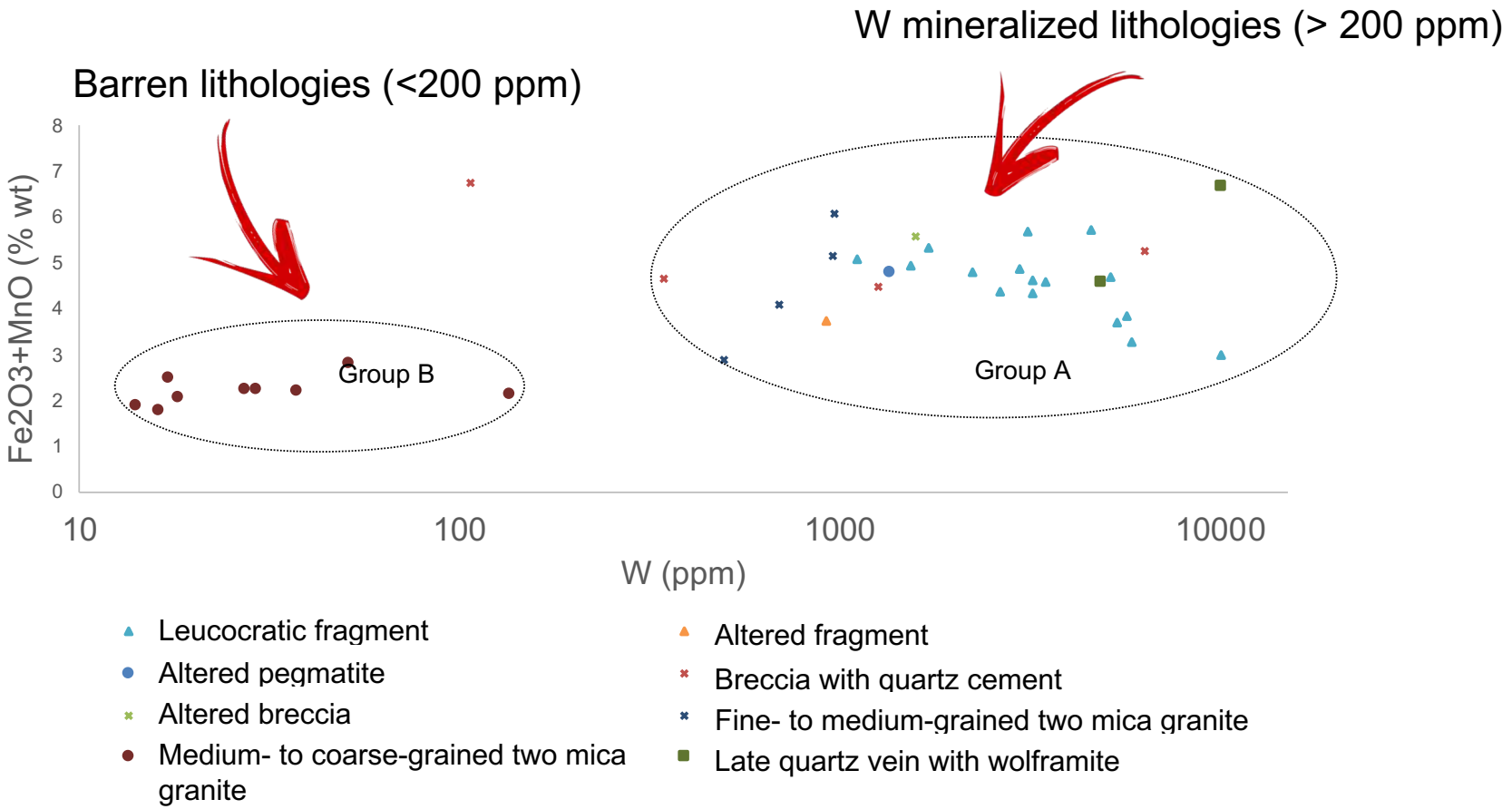

Fig. 9 Fe_2O_3+MnO (% wt) – W (ppm) binary diagram showing composition of lithologies associated with W mineralization (Group A) and the medium- to coarse-grained two mica granite (Group B).

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Geochemical characterization of the Santa Helena breccia

Major element geochemistry

- The major element composition of the studied lithologies shows a **clear increase of some elements in mineralized lithologies** compared with the barren ones:
  - **FeO_{total}, MnO and MgO** suggesting the presence of disseminated **wolframite** ($(Fe,Mn)WO_4$) and **chlorite**;
  - Higher values of **CaO** can suggest the existence of **scheelite**;
  - **K_2O and Al_2O_3** associated with the hydrothermal alteration characterized by a **potassic hydrothermal alteration**.

Table 1. Minimum (min) and maximum (max) major element composition (% wt) of lithologies associated with tungsten mineralization (mineralized) and non-associated with tungsten mineralization (barren).

Element (% wt)	Mineralized (min-max)	Barren (min-max)
SiO_2	67.1-75.7	71.7-76.1
Al_2O_3	12.3-17.4	13.9-14.45
F_eO_{total}	2.38-4.86	1.61-2.38
CaO	0.21-1.25	0.49-0.71
MgO	0.40-1.33	0.25-0.42
Na_2O	0.18-2.69	1.07-2.85
K_2O	3.71-4.98	3.43-4.73
TiO_2	0.16-0.71	0.12-0.2
MnO	0.05-0.19	0.03-0.04
P_2O_5	0.12-0.61	0.35-0.44

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Geochemical characterization of the Santa Helena breccia

Trace element geochemistry

- **Two distinct behaviours (G1 and G2):**
  - G1 - lithologies present in mineralized zones enriched in Ba, Nb, Zr, Sn and W
  - G2 – lithologies present in barren zones
  - Rb and Sr do not show a distinct variation

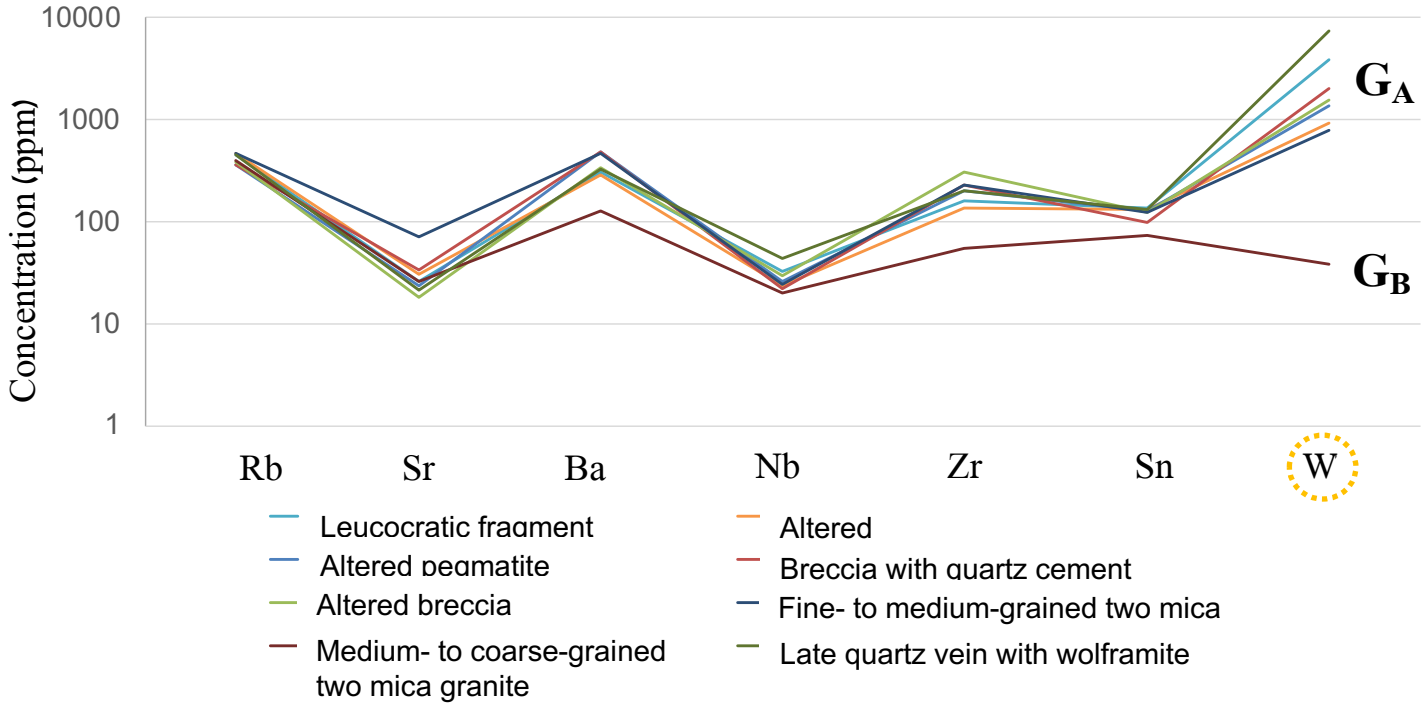

Fig. 10 Trace element variation diagram for the lithologies presented in distinct zones of SHB. Colours used are the same that in fig. 9.

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Mineralization stages

- It must be emphasized that in the present study **only the dispersed mineralization was studied because is typical of the breccia**.
- The previously petrographic observations led to the definition of **four mineralization stages**:
  - *Stage I* (Ti–Sn-W- REE);
  - *Stage II* (W ± Nb-Ta);
  - *Stage III* (Fe-Cu-Zn ± Mo ± Sn);
  - *Stage IV* (Bi ± Pb ± Te-Ag).

See:

Gonçalves et al., 2016 – WES

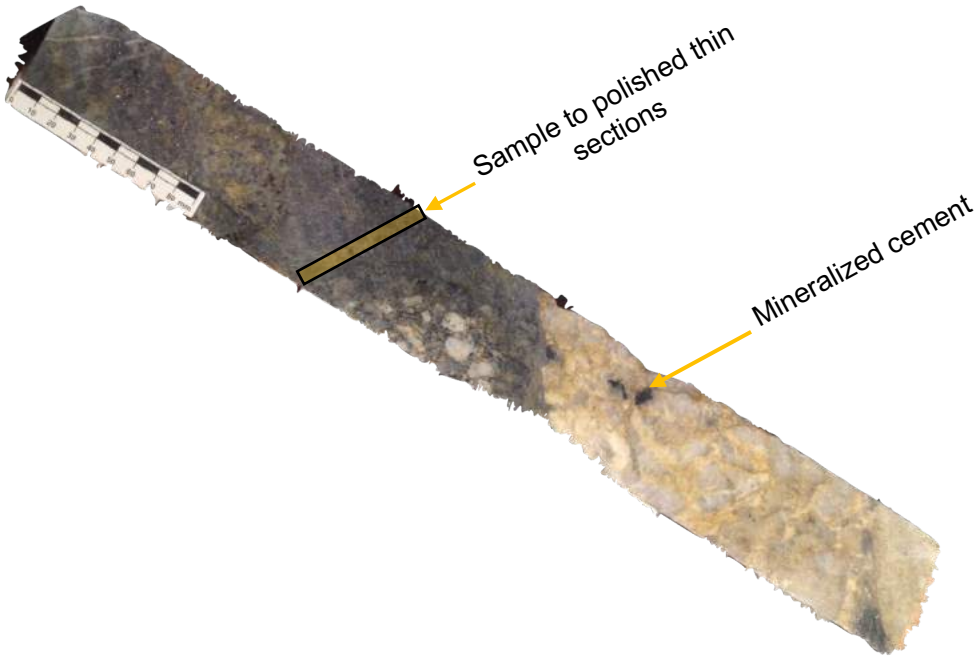

Fig. 11 Representative sample of SHB (provided by Blackheath & Mineralia, Lda).

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Stage I (Ti – Sn – W – REE)

***Stage I* - ilmenite ± cassiterite I ± apatite ± REE phosphates ± scheelite I ± muscovite I ± Fe, Mn chlorite ± biotite ± quartz I**

- Ilmenite superimposed on the quartz (Qtz) and muscovite I (Ms I);
- Small crystals of cassiterite also occur associated with muscovite I;
- Apatite with inclusions of monazite, zircon and U, Th, Y, REE phosphates;
- First generation of scheelite (Sch I) occurs in sub-euhedral well-developed crystals associated with Fe, Mn chlorite in a muscovite I and II + quartz cement.

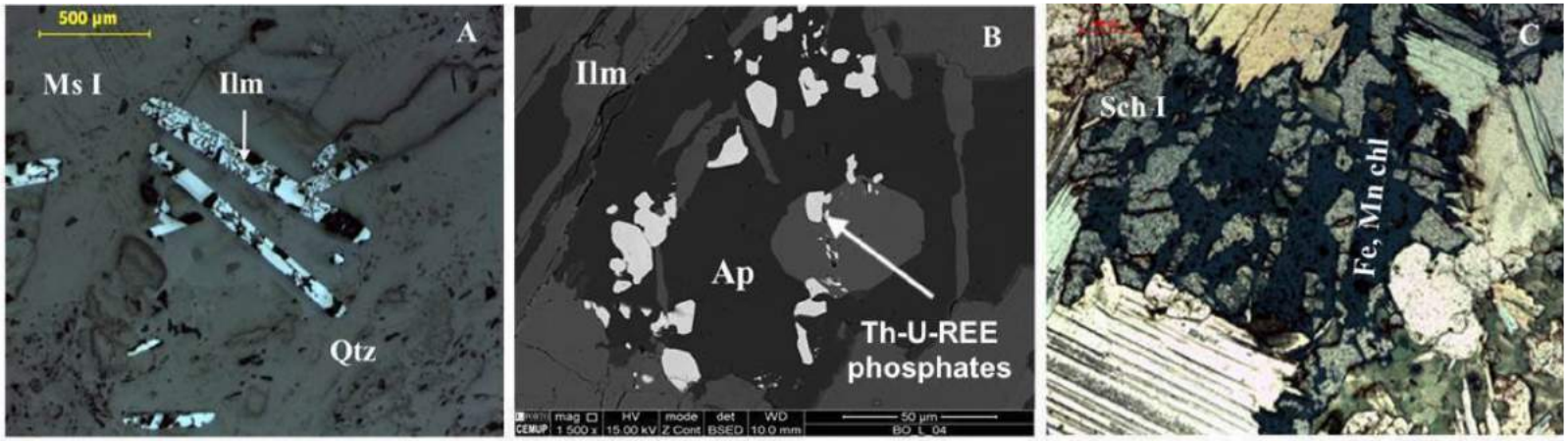

Fig. 12 A. Microphotography in reflected polarized light (RPL) of Ilm (>500 µm) associated with Qtz ± Ms I. **B**. Backscattered electron (BSE) image showing the occurrence of fine Th-U-REE phosphates (≈10 µm) as inclusions partially elongated and parallel to the apatite b axis. **C**. Microphotograph in transmitted light (TL) of Sch I (≈500 µm) associated with Fe, Mn Chl (≈500 µm) in a Qtz ± Ms I (>500 µm) matrix.

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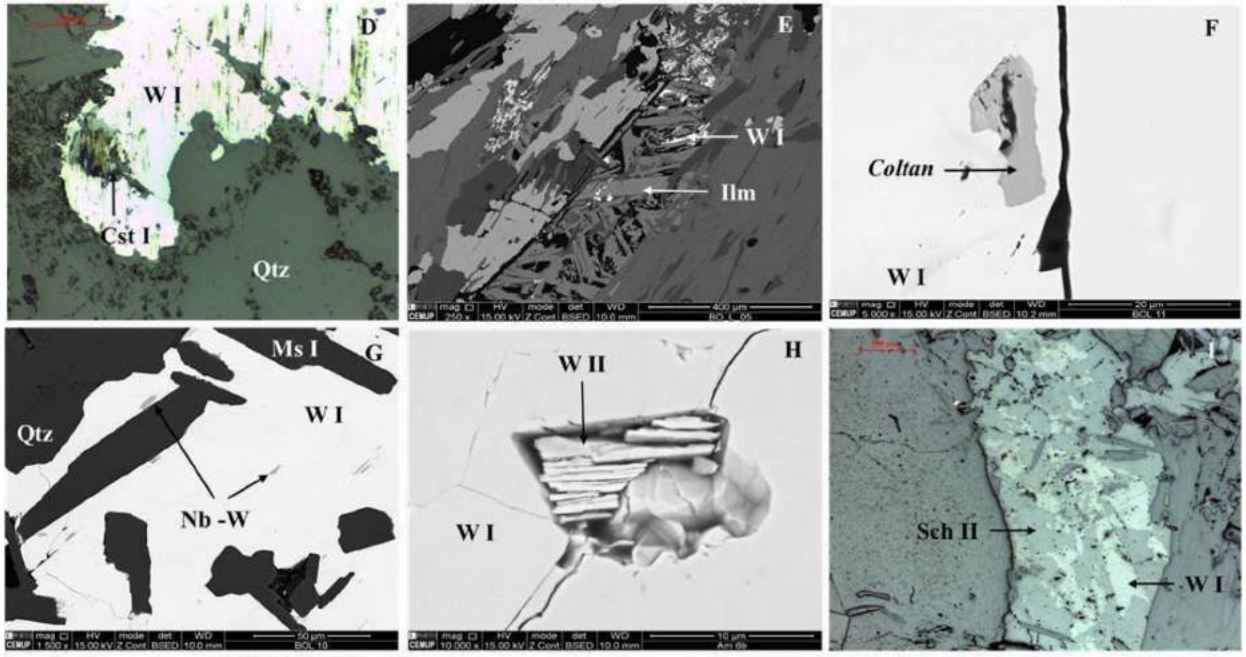
Stage II (W ± Nb-Ta)

***Stage II* - wolframite (I and II) ± scheelite II ± Nb-W oxides ± muscovite II ± Fe chlorite ± quartz II**

- W I present several modes of occurrence and it can contain fine inclusions of Nb-W oxides, coltan, monazite and fluorite. Associated with W I can occur Sch II in anhedral crystals.
- W II occurs in small zoned euhedral crystals filling late fractures and/or cavities in W I.



(***Cont.***) **Fig. 12 D**. Microphotograph in RPL showing the association between W I (, >500 µm) and Cst I (≈200 µm). **E**. BSE image showing a replacing of Ilm by W I. **F**. BSE image showing very fine columbo-tantalite (Coltan ≈20 µm) as inclusion in W I. **G**. BSE image of W I (> 100 µm) with fine inclusions of Nb-W oxides (≈20 µm) randomly scattered showing a preferential orientation. **H**. BSE image of layered W II (≈20-30 µm) filling cavities in W I. **I**. Microphotograph in RPL of Sch II (≈200 µm) associated with W I (≈200 µm) in a Qtz ± Ms I (≈ 500 µm) matrix.

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(*cont.*) Stage II (W ± Nb-Ta)

***Stage II* - wolframite (I and II) ± scheelite II ± Nb-W oxides ± muscovite II ± Fe chlorite ± quartz II**

- The W I presents a MnO average content 5.74%, and **W II is characterised by an enrichment in MnO** (14.495%), consequently, a **composition more huebneritic**;
- The **2 generations of scheelite exhibit similar composition**, however, Sch I presents some MnO (0.065%) and Sch II some FeO (0.118%);
- The **Nb-W exhibits a complex geochemical composition** where the most important oxides are: Nb_2O_5 (56.846%), WO_3 (13.72%), MnO (12.045%), FeO (8.153%), TiO_2 (3.753%) and Ta_2O_5 (3.527%).

See Gonçalves and Noronha, 2017 - Goldschmidt2017

Elements	Sch I	Sch II	W I	W II	Nb-W
Al_2O_3	-	-	-	-	0.011
FeO	-	0.118	17.03	9.7	8.153
CaO	18.85	19.19	0.059	0.07	0.039
MgO	-	-	-	-	0.094
TiO_2	-	-	-	-	3.753
MnO	0.065		5.74	14.495	12.045
P_2O_5	-	-	-	-	0.028
BaO	-	-	-	-	0.048
Nb_2O_5	-	-	0.055	0.054	56.846
SnO_2	-	-	-	-	0.971
Ta_2O_5	-	-	0.515	0.213	3.527
V_2O_3	-	-	-	-	0.019
WO_3	80.91	79.9	75.8	75.29	13.720
PbO	-	-	-	-	0.034
ZnO	-	-	-	-	0.028
NiO	-	-	-	-	0.015
Sc_2O_3	0.036	-	0.037	0.018	-
ZrO_2	-	-	-	-	0.372
SO_3	-	-	-	-	0.073
TOTAL	99.861	99.208	99.236	99.84	99.776

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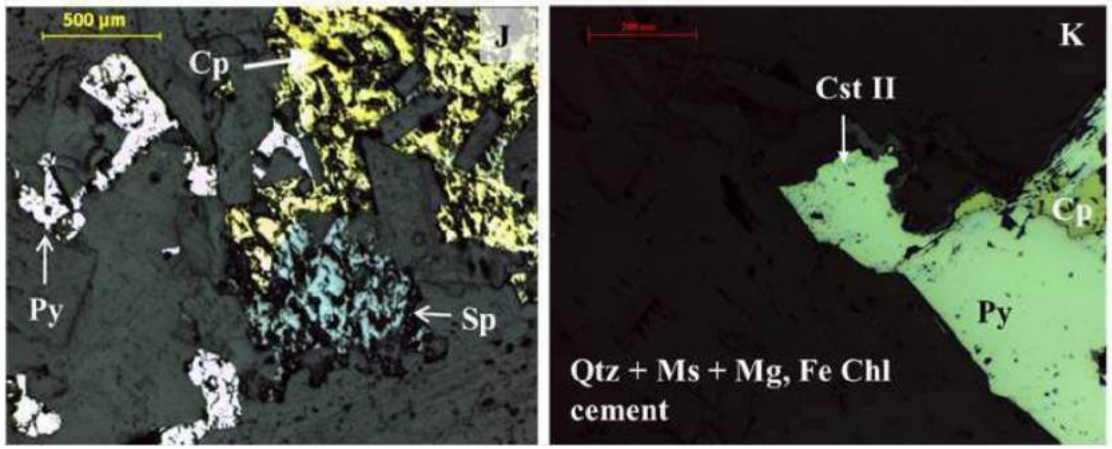
Stage III (Fe-Cu-Zn ± Mo ± Sn)

***Stage III* - cassiterite II ± major sulphides (pyrite ± chalcopyrite ± sphalerite) ± Mg, Fe chlorite**

- It was possible to observe the contemporaneousness between the main sulphides, namely pyrite, chalcopyrite, sphalerite, Mg, Fe chlorite and adularia;
- The main sulphides occur associated with pre-existing Ms I and II ± Qtz and, it is possible to identify rare small crystals of molybdenite;
- Cst II occurs filling latter fractures.



(***Cont.***) **Fig. 12** J. Microphotograph in RPL showing the relationship between Py (≈500 µm), Cp (>500 µm)) and Sp (≈500 µm). K. Microphotograph in RPL of Cst II (≈200 µm) crystallized in the rim of the major sulphides (Py, >500 µm and Cp, ≈ 100 µm).

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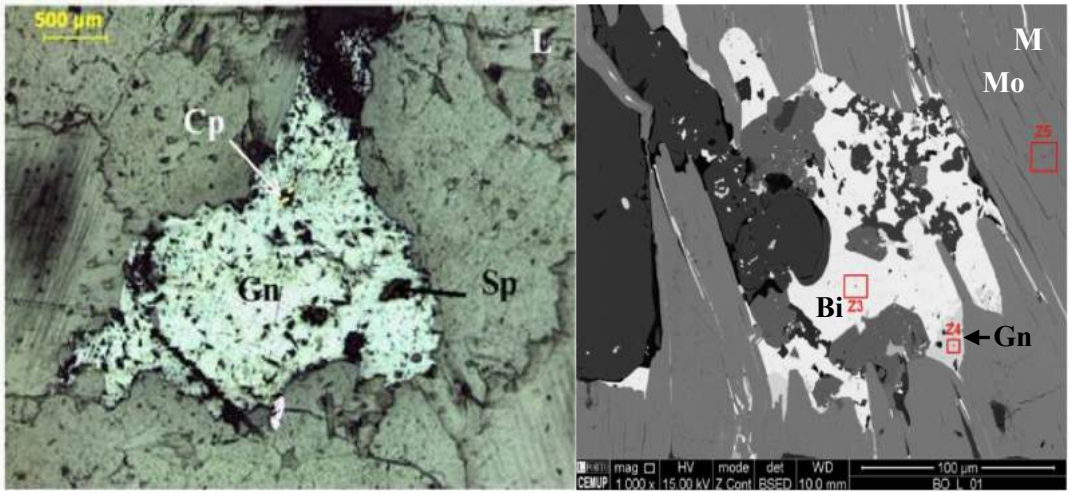
Stage VI (Bi ± Pb ± Te-Ag)

***Stage IV* - native bismuth ± minor sulphides (molybdenite ± bismutinite ± galena ± matildite ± aikinite ± pavonite ± stannite ± greenockite) ± Fe, Mg chlorite ± quartz III.**

- Scarce and fine- grained occurrences of native Bi, galena and Bi-Te-Ag sulphosalts;
- The Bi-Te-Ag sulphosalts fill fractures or voids in major sulphides;
- Coarse-grained of galena with inclusions of chalcopyrite and several small inclusions of sphalerite associated with Fe, Mg chlorite can be observed.



(***Cont.***) **Fig. 12 L.** Microphotograph in RPL showing a mineral phase of Gn (>500 µm) with inclusions of Cp and Sp. **M**. Association between Mo (> 200 µm), native bismuth (Bi, ≈ 100 µm) and Gn (< 50 µm).

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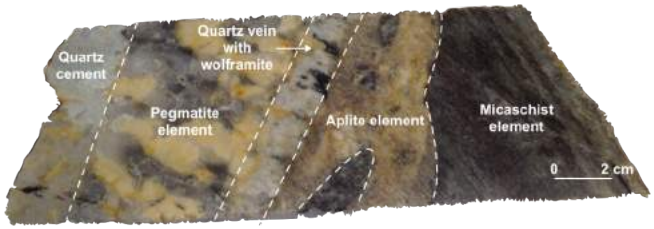
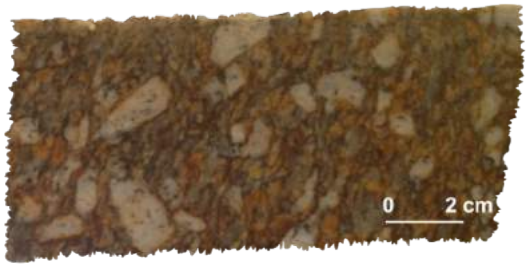
Hydrothermal alteration in hand samples



Santa Helena breccia with mineralized cement composed by quartz and/or a **fine-grained muscovite rich**.



Borralha porphyritic biotite granite element with **oxidation**.

Muscovite rich leucocratic rock mineralized with fine dispersed wolframite

Unaltered two-mica regional granite

Fig. 13 Representative sample of altered and unaltered lithologies from SHB.

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Hydrothermal alteration in polish thin-sections

Main features

- **The main hydrothermal alteration is characterized by muscovite I ± quartz II ± muscovite II ± chlorite** (Fig A).
  - K-feldspar and plagioclase is partially replaced by quartz II ± muscovite II (Fig B).
  - Biotite is replaced by chlorite (Fig C).

Muscovite features

- Muscovite I occur in well-developed crystals (>500 µm);
- Muscovite II is characterized by small crystals (<100 µm) agglomerates with a preferential oriented aspect.

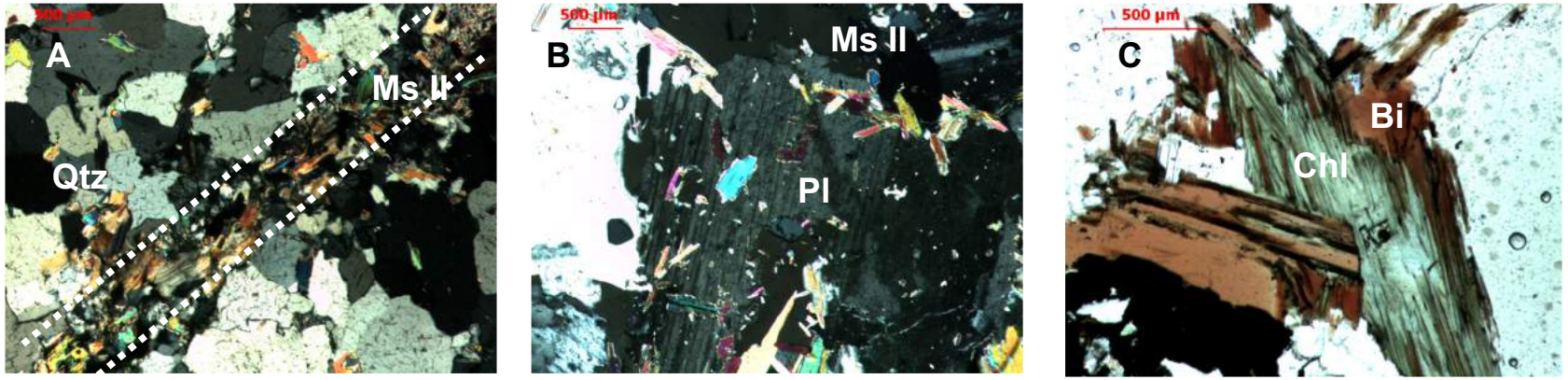

Fig. 14 Hydrothermal alteration typical of SHB.

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Distribution and mobility of REE during the hydrothermal alteration

Accessory REE bearing minerals (See Gonçalves and Noronha, 2017 – CNG)

- **Apatite** occur as euhedral to sub-euhedral crystals associated with biotite and/or as inclusion in quartz I, ilmenite and pyrite.
- Apatite contain fluid inclusions and minor mineral phases (**monazite, xenotime and other REE phosphates**).
- **Monazite** can occur in moderated-sized and/or very small inclusions and in acicular crystals associated with ilmenite.
- **Th-U phosphates** occur as fine elongated inclusions parallel to the apatite *b* axis.

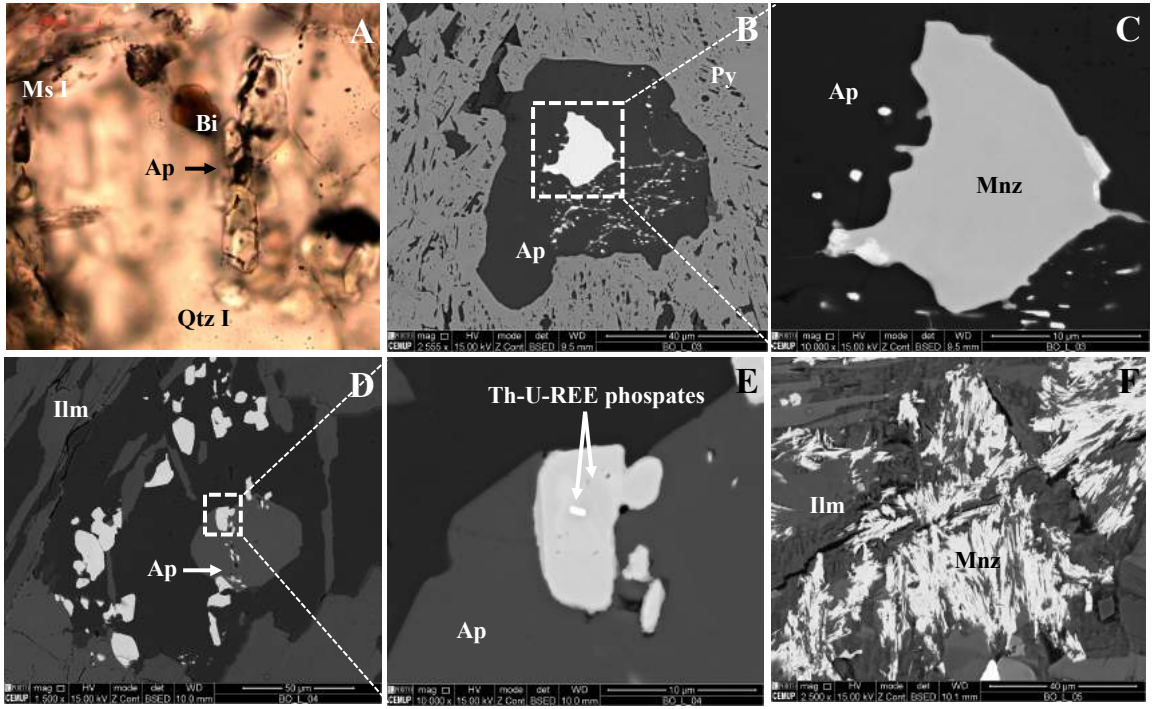

Fig. 15 A. Microphotograph in transmitted light showing the occurrence of the main REE bearing mineral phases.

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Distribution and mobility of REE during the hydrothermal alteration

Breccia (n=8) – altered samples

- 159.2 < ΣREE < 309 ppm
- $LREE_{mean}$ of 209.09 ppm and $HREE_{mean}$ of 13.26 ppm

Porphyritic biotite granite (Borralha granite, *n*=2)

50 – altered sample: ΣREE =134.7 ppm

Bor1 – unaltered sample: ΣREE = 101.5 ppm

Two-mica fine-grained peraluminous granites (*n*=2) – unaltered samples

- 40.0 < ΣREE < 48.7 ppm

Two-mica medium grained peraluminous granite (*n*=1) – unaltered sample

- ΣREE=58.6 ppm

The mean contents in REE (222.34 ppm) of the breccia are always higher than in the regional granites.

Samples	18	28	56	67	89	96	167	169	183	184	50	91	Bor1
La	71.4	83.8	31.3	38.9	38.8	38.8	47.3	54.9	62.2	9.9	7.9	12.0	21.22
Ce	130.5	143.5	64.1	77.1	74.8	80.8	98.5	109.5	124.0	21.1	17.3	27.3	45.35
Nd	55.7	56.6	25.3	31.0	30.1	33.7	39.3	43.0	45.8	9.0	7.4	11.3	21.65
Sm	9.1	9.0	4.4	4.9	4.5	5.8	6.5	7.4	7.6	2.8	2.2	2.7	4.97
Eu	1.4	1.3	0.7	0.8	0.8	0.9	0.8	0.8	1.1	0.3	0.2	0.3	0.6
Gd	7.1	6.2	3.4	3.7	3.7	4.7	5.3	5.3	5.4	2.7	2.2	2.3	3.88
Dy	5.2	4.4	2.7	3.2	3.1	4.3	4.1	3.7	3.8	1.9	1.8	1.4	2.22
Er	2.4	2.0	1.4	1.4	1.7	2.4	2.3	1.7	2.2	0.6	0.6	0.8	0.81
Yb	1.8	1.9	1.2	1.5	1.5	2.2	2.1	1.7	1.9	0.4	0.4	0.4	0.68
Lu	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.1	0.16	0.1	0.11
La*	291.9	342.6	128.0	159.0	158.6	158.6	193.4	224.4	254.3	40.5	32.3	49.1	86.8
Ce*	204.6	225.0	100.5	120.9	117.3	126.7	154.4	171.7	194.4	33.1	27.1	42.8	71.1
Nd*	117.6	119.5	53.4	65.4	63.5	71.1	82.9	90.8	96.7	19.0	15.6	23.8	45.7
Sm*	58.9	58.7	28.4	31.6	29.2	37.7	42.3	48.1	49.4	17.9	14.4	17.5	32.3
Eu*	23.3	22.4	12.2	14.0	14.3	15.2	14.3	14.5	19.6	5.0	4.0	5.2	10.3
Gd*	34.9	30.2	16.7	18.2	18.0	23.0	26.0	25.9	26.3	13.0	10.7	11.3	19.0
Dy*	20.3	17.3	10.7	12.6	12.1	16.9	16.1	14.7	15.0	7.6	7.0	5.5	8.7
Er*	14.4	12.1	8.3	8.6	10.1	14.2	13.9	10.4	13.1	3.8	3.6	4.8	4.9
Yb*	10.7	11.3	7.5	9.0	8.9	13.6	12.4	10.5	11.5	2.4	2.3	2.4	4.1
Lu*	9.8	11.4	6.3	8.3	10.6	11.8	12.2	10.2	11.8	2.0	1.6	3.9	4.33
LREE	268.0	294.2	152.7	149.0	160.0	192.4	215.7	240.7	43.0	35.0	125.8	53.6	93.8
HREE	16.7	14.7	10.1	10.2	13.9	14.1	12.8	13.6	5.7	5.0	8.9	5.0	7.7
∑REE	284.7	309.0	162.8	159.2	173.9	206.5	228.4	254.3	48.7	40.0	134.7	58.6	101.5
Eu/Eu*	0.5	0.5	0.6	0.6	0.5	0.4	0.4	0.5	0.3	0.3	0.5	0.4	0.4
Eu/Eu	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.14
La/Sm	7.9	9.3	8.0	8.6	6.7	7.3	7.4	8.2	3.6	3.6	7.1	4.4	4.27
La*/Sm*	5.0	5.8	5.0	5.4	4.2	4.6	4.7	5.2	2.3	2.3	4.5	2.8	2.69
Gd/Yb	4.0	3.3	2.5	2.5	2.1	2.6	3.0	2.8	6.6	5.7	2.8	5.8	5.71
Gd*/Yb*	3.3	2.7	2.0	2.0	1.7	2.1	2.5	2.3	5.4	4.6	2.2	4.6	4.61
La/Yb	40.3	44.8	26.1	26.4	17.3	23.1	31.6	32.7	24.8	20.8	25.4	30.0	3.21
La*/Yb*	27.2	30.2	17.6	17.8	11.7	15.6	21.3	22.1	16.7	14.0	17.2	20.2	21.06

LREE: La-Gd and HREE: Dy-Lu
– normalised to the chondrite contents (Evensen *et al.*, 1978)

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Distribution and mobility of REE during the hydrothermal alteration

Similar profiles but two distinct behaviours:

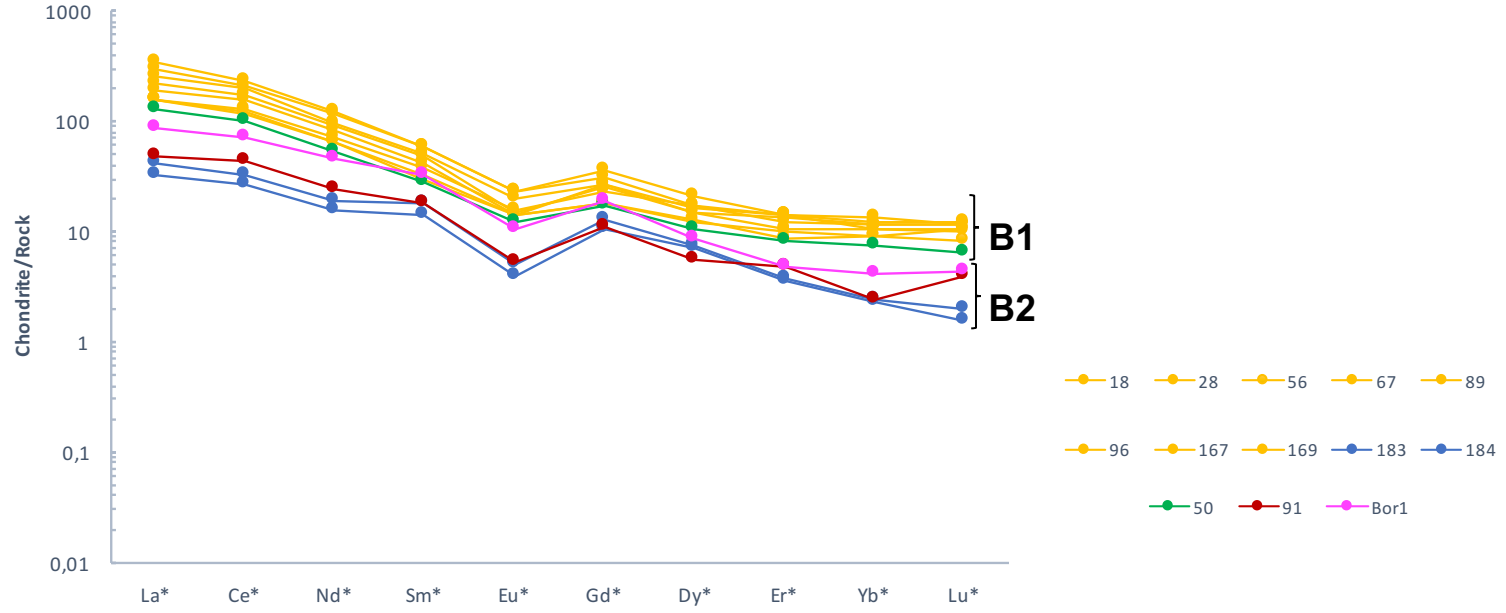
- **Altered rocks - enriched in REE (B1);**
- **Unaltered rocks (B2).**

Interpretation:

- Altered rocks (breccia samples) exhibit higher normalised values in REE (namely LREE) than unaltered rocks.

- Porphyritic biotite granite (altered and unaltered) present similar behaviour; however, the unaltered sample (Bor1) present a amount in REE lower than the altered sample (50).

- The unaltered two-mica granites is depleted in REE if we compare with the altered samples.



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Main Conclusions

- Four mineralization stages were defined, proving **four independent periods of ore deposition for a disseminated fine to medium-grained mineralization** in the breccia pipe;

- **The geochemical composition of the mineralized zones shows an increase of MnO, Fe_2O_3, MgO, Al_2O_3, K_2O, Ba, Nb, Zr, Sn, W as well as REE** compare to barren zones;

- The **hydrothermal alteration** appears with variable intensity and is characterized firstly by **muscovite I and, after, by quartz I ± muscovite II ± chlorite**;

- Cluster analysis and Perason's correlation coefficients for **trace elements and REE showed a strong affinity** ($r_{strong}>0.5$, $p<0.05$), corresponding to the occurrence of **apatite, monazite, xenotime and Th-U phosphates**;

- **Apatite is the most common REE-bearing** accessory mineral and contain other REE-bearing minerals, such as monazite, xenotime and other Th-U-REE phosphates, as "exsolution" resulting from later concentration processes;

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Main Conclusions

- **REE can be considered mobile during the fluid-rock interaction related to magmatic-hydrothermal fluids**, associated with a buried cupola of a late-orogenic granite, that implies a **W, Ti, Sn, P, Th, U, REE mineralization**.

- A mineral association characterized by a low content of sulphides and total volume of 40-50 Mt and **22.5 Mt with a grade average of 750 g/t WO_3 are favourable;**

- The breccia pipe represents a late-Variscan W (Sn, Nb, Ta, REE) mineralization suggesting a **magmatic-hydrothermal history related with a magmatic intrusion still unknown at depth**.

- The presence of **disseminated W mineralization** with **high grades** and the **large volume** of SHB pipe, allows the exploitation in **open pit**.

- The exploitation of a "**Critical Metal**" in a destitute region of **Portugal** would be crucial to improve the economic and social development.

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Publications

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Santa Helena Breccia Pipe (Borralha): A new type of tungsten ore deposit in Northern Portugal

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Abstract

Borralha is located in Northern Portugal and is a past producer of tungsten. It was the second largest tungsten mine in Portugal after Panasqueira tungsten mine until its closure in 1985. In Borralha underground tungsten mine, the mineralization was exploited from vertical and sub-horizontal quartz veins with wolframite, scheelite and sulphide mineralization. In addition to the vein structures, there also occur two breccias bodies: Santa Helena (the largest) and Venise. Only the first one outcrops and was partially mined in the 50's, because it has tungsten mineralization, both in cement and in ore shoots. In former times, there was a preferred exploitation near the two quartz veins that limit the breccia at east and west and also of the veins known outside the breccia and that were possible to follow inside the structure. The Santa Helena breccia is a sub-vertical Variscan structure is exposed at surface and detailed historical underground mapping and surface geological mapping indicate it may be at least 575 m in length, over 150 m in width and open to a depth of over 200 m. The major axis has a strike close to N-S. The fragments of the breccia are mainly angular and their sizes are very variable. It is possible to find side by side metric blocks next to centimetric fragments. The lithological composition of fragments is identical to the surrounding rocks, i.e., granite, tonalite, pegmatite and schists. The breccia elements exhibit hydrothermal alteration with variable intensity and mainly occurring near the contact of the breccia elements with the cement and being characterized by an enrichment on muscovite + quartz associated with secondary fracturing associate with fine dispersed mineralizations. However, we can recognize the existence of veinlets within the breccia. During 2013-2014, trenches, channels and 9 drills were carried out by the consortium Blackheath & Mineralia for evaluation of Santa Helena breccia. In all the cases were intercepted disseminated fine wolframite and scheelite, mainly in the altered granitic elements. Despite the frequent presence of fine tungstates disseminated along the drill holes, there are intervals where larger wolframite crystals are visible associated with quartz veinlets and consequently with higher grades proved by geochemical assaying. In the drill holes was also possible to identify some sulphides usually associated with chlorite. The present work contributes to the mineralogical study of this atypical tungsten deposit and allows the definition and identification of successive mineralization stages different from that of the quartz veins that were exploited till 1985. Several analytical techniques were used for their identification, namely, optical microscopy, scanning electron microscopy, electron microprobe and geochemistry. Different deposition stages were identified: (I) stage with ilmenite, cassiterite I, monazite, Th-U, REE phosphates and minor xenotime; (II) W-Nb stage with wolframite, scheelite and Nb-W oxides; (III) Fe-Cu-Zn ± Mo ± Bi ± Ag ± Pb stage with sulphides of base metals such as pyrite, chalcopyrite, sphalerite and minor stannite, molybdenite, matildite, greenockite, native bismuth, galena and a mineral phase with Ag and Te all associated with chlorite. A latter cassiterite II is found.The results prove that mineralization and grades are dispersed, however a N-S central sector exhibits higher grades. A total volume of 24Mt was defined in the breccia just to the level -110.

Acknowledgements: Work financially supported by (FCT Portugal). Project ERAMIN-NewOreS "Development of new models for the genesis of Rare Metal (W, Sn, Nb, Ta, Li) ore deposits from the European Variscan Belt and valorisation of low grade and fine-grained ore and mine tailings".

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ACKNOWLEDGEMENTS

Work financially supported by (FCT Portugal). Project - NewOres "Development of new models for the genesis of Rare Metal (W, Sn, Nb, Ta, Li) ore deposits from the European Variscan Belt and valorization of a low grade and fine-grained ore and mine tailings" (ERA-MIN/ 0002/2014).

ABSTRACT

The ore deposit of Borralha was exploited during the twentieth century mainly from vertical and sub-horizontal quartz veins with wolframite, scheelite and sulphide mineralization. In addition to the vein structures, there also occur two breccias bodies: the **Santa Helena breccia (SHB)** and Venise breccia. The present work aims to contribute to the study of the SHB, an atypical tungsten deposit. There are several hydrothermal alterations with variable intensity, mainly occurring near the contact elements-quartz cement and in late fractures, which are characterized firstly by are muscovite and after by quartz ± sericite. Occurrences of chlorite characterize the last hydrothermal alteration. Different mineralization stages can be identified: I) ilmenite ± cassiterite I ± Th-U-REE phosphates ± muscovite; II) wolframite ± scheelite ± Nb-W oxides; III) sulphides of base metals (pyrite, chalcopyrite, sphalerite and cassiterite II) and minor stannite, molybdenite, matildite, greenockite, bismutinite, native bismuth, galena and Ag-Te sulphide. This stage is associated with chlorite.

INTRODUCTION

The Variscan cycle is associated in the Iberian Peninsula with the deposition of a wide variety of metallic and non-metallic mineral resources. A large number of tungsten deposits and occurrences are present in the northwest of the Iberian Peninsula. The hydrothermal W (Sn) mineralizations were conditioned by Variscan structures and alignments. Tungsten mineralization can be found on the contact between granites and metasedimentary rocks and on the contact between granites with different ages [1]. The Borralha deposit was mined until 1985; the mineralization was exploited, in underground works, from vertical and sub- horizontal quartz veins with wolframite, scheelite and sulphide mineralization and from a breccia in open pit (SHB). The total production of wolframite and scheelite concentrates has been estimated at about 18500 tonnes of WO_3 [2].

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Santa Helena Breccia Pipe (Borralha): a new type of tungsten ore deposit in Northern Portugal

Gonçalves, A.,[a*] Lima, L.,[b] Mota, A.,[b] Ramos, V.,[a] Barros, J.,[c] Noronha, F.[a,b]

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THE SANTA HELENA BRECCIA

The SHB is located in the contact between the Central Iberian Zone (authoctonous terranes) and the northwestern part of Galiza-Trás-os-Montes zone (parauthoctonous terranes) in Borralha area (Montalegre). It corresponds to a sub-vertical structure cutting the contact between a sintectonic biotite granite (Borralha granite) and metasedimentary rocks (Silurian in age) (FIGURE 1). The fragments of the breccia are mainly angular and their sizes are very variable. The pipe has been interpreted as a collapse breccia [3,4]. The lithological composition of the clasts is identical to the surrounding rocks, i.e., granite, tonalite, pegmatite and schists. The mineralization is, in general, fine, dispersed in the breccia elements, in cement and secondary fracturing. It is characterized by the association of W, Cu, Zn, Mo and minor Nb, Sn, Th, U, REE, Bi, Ag, Pb. However, we can recognize the existence of late veinlets with coarse W mineralization cutting the breccia.

MATERIALS AND ANALYTIC METHODS

During 2013-2014, trenches, channels and nine drills were carried for the evaluation of SHB (FIGURE 2A). Two drill cores were selected, **Bo_5/14** and **Bo_8a/14** (FIGURE 2B).

Several analytical techniques were used:

- ❖ optical microscopy;
- ❖ scanning electron microscopy (SEM-EDS);
- ❖ geochemistry.

FIGURE 1. Location and geological setting of the Santa Helena breccia in the Borralha area.

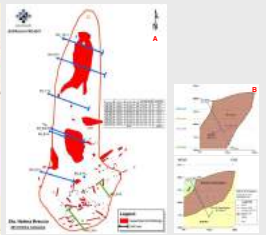

FIGURE 2. A) Completed Drilling of Santa Helena Breccia (SHB). B) Geologic profile from drill holes Bo_5/14 (attitude: 63º→N106º) and Bo_8a/14 (Attitude: 60º→N110º).

RESULTS

I. Occurrence of the mineralization in the cores

- ❖ Disseminated fine wolframite and scheelite, associated with greisenized granitic elements (FIGURE 3A);
- ❖ Fine and medium wolframite associated with quartz cement (FIGURE 3B);
- ❖ Coarser wolframite crystals are visible associated with late quartz veinlets (FIGURE 3C);
- ❖ Sulphides usually associated with vermicular chlorite.

II. Mineralogy

❖***Stage I*** - ilmenite ± cassiterite I ± Th-U-REE phosphates: ilmenite occurs associated with quartz + muscovite (FIGURE 4A). The presence of cassiterite I occurs as inclusions in later minerals like wolframite. In this stage also occur apatite, biotite and very fine REE phosphates (FIGURE 4B). Apatite, in some cases, has inclusions of monazite, zircon and xenotime.

❖***Stage II*** - wolframite ± scheelite ± Nb-W oxides: wolframite occurs associated with quartz + sericite and sometimes appears replacing ilmenite (FIGURE 5A,C). Scheelite is scarcer and occurs most often associated with a lamellar chlorite (Fe, Mn) and wolframite (FIGURE 5B,C). In this stage, it was possible to identify some crystals of latter Nb-W oxides associated with tungstates.

❖***Stage III*** – main sulphides (pyrite, chalcopyrite, sphalerite and cassiterite II): pyrite, chalcopyrite and sphalerite are contemporary (FIGURE 6). A second generation of cassiterite II occurs surrounding pyrite. It was possible to identify some fine phases associated with the main sulphides such as stannite, molybdenite, matildite, greenockite, bismutinite, native bismuth, galena and sulphides with Ag and Te (FIGURE 7A,B) and vermicular chlorite.

FIGURE 3. Ocurrence of mineralization in the cores of Santa Helena breccia. A) Disseminated fine wolframite and scheelite associated with greisenized granitic elements. B) Medium wolframite associated with quartz cement. C) Coarser wolframite crystals are visible associated with late quartz veinlets.

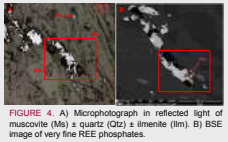

FIGURE 4. A) Microphotograph in reflected light of muscovite (Ms) ± quartz (Qtz) ± ilmenite (Ilm). B) BSE image of very fine REE phosphates.

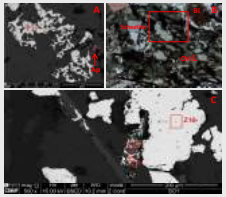

FIGURE 5. A) BSE image of disseminated fine wolframite associated with quartz. B) Microphotograph in transmited light showing the relationship between vermicular chlorite (Chl), biotite (Bi), scheelite and sulphides. C) BSE image of scheelite (Z10) and wolframite (Z11) replacing prior ilmenite (Z12).

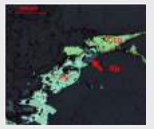

FIGURE 6. Microphotograph in reflected light showing the relationship between pyrite (Py), chalcopyrite (Ccp) and sphalerite (Sp).

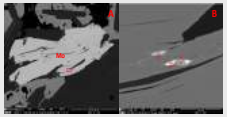

FIGURE 7. A) BES image of a molybdenite crystal (Mo). B) BES image of very fine bismutinite (Z1), Ag-Te sulphides (Z2) and galena (Z3) as inclusions in molybdenite.

CONCLUSIONS

This study allowed identifying **three stages of mineralization in the SHB**: *stage I* - ilmenite ± cassiterite I ± Th-U-REE phosphates; *stage II* - wolframite ± scheelite ± Nb-W oxides; *stage III* - sulphides of base metals (pyrite, chalcopyrite, sphalerite and cassiterite II) and it was possible to identify some fine phases associated with the main sulphides such as stannite, molybdenite, matildite, greenockite, bismutinite, native bismuth, galena and sulphides with Ag and Te and vermicular chlorite. The defined stages are different from the previous defined for quartz veins and correspond to a disseminated type of mineralization representing a new mineralization type in Iberian tungsten Variscan province.

The Santa Helena Breccia Pipe (Borralha – N Portugal): a new mineralization type in Iberian Tin and Tungsten Province

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Abstract **– The ore deposit of Borralha was exploited during the twentieth century mainly from vertical and sub-horizontal quartz veins with wolframite, scheelite and sulphide mineralization. In addition to the vein structures, there also occur two breccias bodies: the Santa Helena breccia (SHB) and Venise breccia. The present work aims to contribute to the study of the SHB, an atypical tungsten deposit. There are several hydrothermal alterations with variable intensity, mainly occurring near the contact elements-quartz cement and in late fractures, which are characterized firstly by are muscovite and after by quartz ± sericite. Occurrences of chlorite characterize the last hydrothermal alteration. Different mineralization stages can be identified: I) ilmenite ± cassiterite I ± Th-U-REE phosphates ± muscovite; II) wolframite ± scheelite ± Nb-W oxides; III) sulphides of base metals (pyrite, chalcopyrite and sphalerite), cassiterite II and molybdenite; IV) minor stannite, matildite, greenockite, bismutinite, native bismuth, galena and Ag-Te sulphide – this stage is associated with chlorite.**

Resumo **- O jazigo de tungsténio da Borralha foi explorado durante o século XX. Nos níveis subterrâneos da mina, o minério de tungsténio foi extraído dos filões verticais e sub-horizontais de quartzo, onde ocorrem volframite, scheelite e sulfuretos. Além das estruturas filonianas mineralizadas, ocorrem, também, dois corpos brechóides com mineralização hidrotermal associada: a brecha de Santa Helena e a brecha Venise. O presente trabalho tem como objetivo principal o contributo para o estudo do depósito mineral atípico da brecha de Santa Helena. Os elementos constituintes da brecha apresentam alteração hidrotermal com intensidade variável. Esta alteração é evidente próximo do contacto entre os elementos da brecha com o cimento quartzoso e em fraturas tardias, sendo caracterizada numa fase inicial por um enriquecimento em moscovite e, posteriormente, em quartzo + sericite. Diferentes estádios de deposição mineral foram identificados: I) ilmenite ± cassiterite I ± fosfatos de terras raras ± moscovite; II) volframite ± scheelite ± óxidos de Nb-W; III) sulfuretos essenciais (pirite, calcopirite e esfalerite), cassiterite II e molibdenite; IV) e com menor expressão, estanite, matildite, greenockite, bismuto nativo, galena e sulfuretos de Ag-Te – este estádio ocorre associado à clorite.**

Key words – Hydrothermal alterations, Santa Helena breccia pipe, Th-U-REE phosphates, Tungsten mineralization.

Introduction

Mineral deposits are extraordinary anomalies in the Earth that provide us with, perhaps, the clearest evidence of the past flow of solutions through faults, fractures and porous rocks that, in the process, dissolved, transported and concentrated elements of economic interest [1]. The Variscan cycle, is associated in the Iberian Peninsula with the deposition of a wide variety of metallic and non-metallic mineral resources. A large number of tungsten deposits and occurrences are present in the northwest of the Iberian Peninsula. The hydrothermal W (Sn) mineralizations were conditioned by Variscan structures and alignments. Tungsten mineralizations can be found on the contact between granites and metasedimentary rocks and on the contact between granites with different ages [2]. In Figure 1 is represented the distribution of the tungsten and tungsten/tin mineralizations (in quartz veins and skarns) in northern Portugal. The Borralha deposit was mined until 1985; the mineralization was exploited, in underground works, from vertical and sub-horizontal quartz veins with wolframite, scheelite and sulphide mineralization and from a breccia were the wolframite mineralization occurred in pockets near the contact veins present in East and West contacts and was exploited in open pits. The total production of wolframite and scheelite (tungsten minerals) concentrates from 1904 until the closing of Borralha was estimated at about 18,500 t, although this number is approximate and may be substantially below than the true value [3].

The Santa Helena Breccia

The SHB is a remarkable occurrence of hydrothermal tungsten mineralization in the west European Variscan Belt and represents a rare type of W deposit because the mineralization is disseminated. It is located in the contact between the Central Iberian zone (autochthonous terranes) and the northwestern part of Galiza-Trás-os-Montes zone (parautochthonous terranes) in Borralha area (Montalegre). It corresponds to a sub-vertical structure cutting the contact between syntectonic biotite granite (Borralha granite) and metasedimentary rocks (Silurian in age) [5]. SHB is exposed at surface and detailed historical underground and surface geological mapping indicate it may be at least 575 m in length, over 150 m in width and at least 200 m in height (known till -110m depth). The major axis has a strike close to N-S (Figure 2). The pipe has been interpreted as a collapse breccia [6]. The fragments of the breccia are mainly angular and their sizes are very variable. It is possible to find side by side metric blocks next to centimetric clasts. The lithological composition of the clasts is identical to the surrounding rocks, i.e., granite, tonalite, pegmatite and schists. There are several hydrothermal alterations with variable intensity, mainly occurring near the contact elements-quartz cement and in late fractures, which are characterized firstly by muscovite and after by quartz ± sericite. An occurrence of chlorite characterizes the last hydrothermal alteration. The mineralization is, in general, fine, dispersed in the breccia elements and in the cement and can also occur in secondary fracturing. It is characterized by the association of W, Cu, Zn, Mo and minor Nb, Sn, Th, U, REE, Bi, Ag, Pb. However, we can recognize the existence of late veinlets with coarse wolframite cutting the breccia.

FIGURE 1. Distribution of W-Sn Deposits in northern Portugal [*adapted* 4]. 1- COVAS; 2- CARRIS; 3- BORRALHA; 4- CRAVEZES; 5- LAGOAÇA; 6- RIBA D'ALVA; 7- STA LEOCÁDIA; 8- S. PEDRO DAS ÁGUIAS; 9- SARZEDAS; 10- BESSA; 11- TURLA; 12- MORÇÓS; 13- RIBEIRA; 14- ARGOZELO; 15- ADORIA; 16- VALE DAS GATAS; 17- FREIXO DE NUMÃO; 18- TAROUCA; 19- ALMENDRA; 20- REGOUFE; 21- LAGARES; 22- AZEVO; 23- BEJANCA; 24- GÓIS; 25- PANASQUEIRA; 26- MATA DA RAINHA; 27- SEGURA.

Materials and Analytic Methods

During 2013-2014, trenches, channels and nine drills were carried out by the consortium Blackheath & Mineralia for the evaluation of SHB. For this study two drill cores were selected, Bo_5/14 and Bo_8a/14, because they were considered representative of the breccia and corresponding mineralization (Figure 3). Several analytical techniques were used in this study: optical microscopy, scanning electron microscopy (SEM-EDS) and geochemistry. Petrographic observations of polished thin-sections were performed at the Faculty of Sciences, University of Porto, using a stereomicroscope Zeiss Stemi SV11 Apo coupled with a Sony Cyber-Shot DSC-S75 digital camera and also using a Leica DM LSP polarizing microscope, with transmitted and reflected light, coupled with a Leica camera with LAS EZ software 2.0.0. SEM-EDS analyses were performed at CEMUP (Materials Centre of the University of Porto, Portugal) using an FEI Quanta 400 FEG-ESEM/EDAX Genesis X4M instrument. The SEM was operated at 15 kV in high-vacuum mode, manual aperture, and 4.5 beam spot sizes. The chemical analyses of each core were performed at ALS Laboratory Group, SL in Seville (Spain).

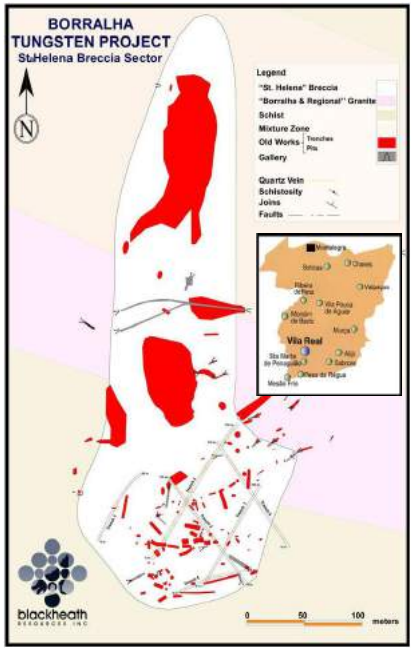

FIGURE 2. Location and geological setting of the Santa Helena breccia in the Borralha area [3].

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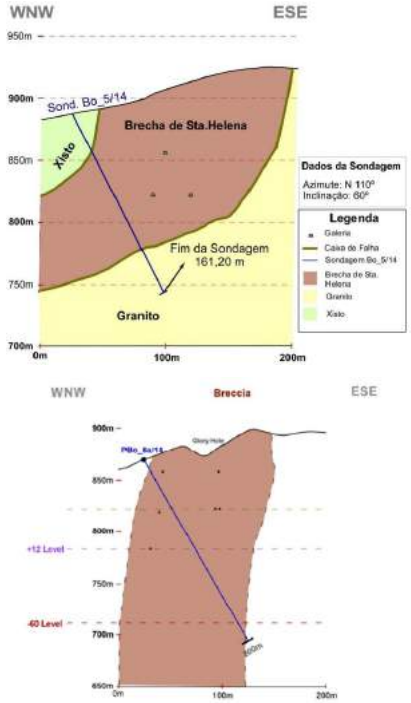

FIGURE 3. GEOLOGIC PROFILE FROM DRILL HOLES BO_5/14 (ATTITUDE: 63º→N106º) AND BO_8A/14 (ATTITUDE: 60º→N110º).

RESULTS

I. Occurrence of the mineralization in the cores

The sampling of SHB allowed to identify disseminated fine wolframite and scheelite, mainly in the greisenized granitic elements and medium wolframite associated with the cement (Figure 4A,B). Despite the frequent presence of fine and medium tungstates disseminated along the drill holes, there are intervals where larger wolframite crystals are visible associated with late quartz veinlets (Figure 4C) and consequently with higher grades. In the drill holes was also possible to identify some sulphides usually associated with vermicular chlorite.

II. Mineralogy

This work presents results concerning the mineralogy of SHB. According to [7,8] and to new petrographic observations, the paragenetic sequence of the SHB deposit can be divided into four stages.

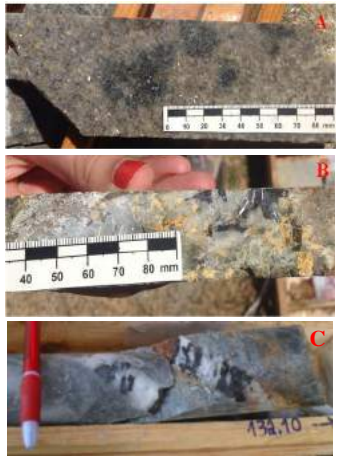

FIGURE 4. MINERALIZATION TYPES IN SHB. A. DISSEMINATED FINE WOLFRAMITE AND SCHEELITE, MAINLY IN THE GREISENIZED GRANITIC ELEMENTS (WO_3= 4453 ppm, DEPTH: 109 m). B. DISSEMINATED MEDIUM WOLFRAMITE ASSOCIATED WITH QUARTZ CEMENT ($W0_3$=19176 ppm, DEPTH: 150 m). C. COARSE WOLFRAMITE CRYSTALS ASSOCIATED WITH LATE QUARTZ VEINLET (WO_3 =12616 ppm, DEPTH: 132 m).

Stage I - ilmenite ± cassiterite I ± Th-U-REE phosphates: ilmenite occurs associated with quartz + muscovite (Figure 5A). The presence of a cassiterite I occurs as inclusions in later minerals like wolframite. In this stage also occur apatite, biotite and very fine REE phosphates. Apatite, in some cases, has inclusions of monazite, zircon and xenotime.

Stage II - wolframite ± scheelite ± Nb-W oxides: wolframite occurs associated with quartz + sericite and sometimes appears replacing ilmenite (Figure 5B,D). Scheelite is scarcer and occurs most often associated with a lamellar chlorite and wolframite (Figure 5C). In this stage, it was possible to identify some crystals of late Nb-W oxides associated with tungstates (Figure 5E).

Stage III – main sulphides (pyrite, chalcopyrite and sphalerite) and cassiterite II: pyrite, chalcopyrite and sphalerite are contemporary (Figure 5F). A second generation of cassiterite (cassiterite II) occurs surrounding pyrite (Figure 5G).

Stage IV - Minor stannite, molybdenite, matildite, greenockite, bismutinite, native bismuth, galena and sulphides with Ag and Te: it was possible to identify some fine phases associated with the main sulphides (Figure 5H) and vermicular chlorite.

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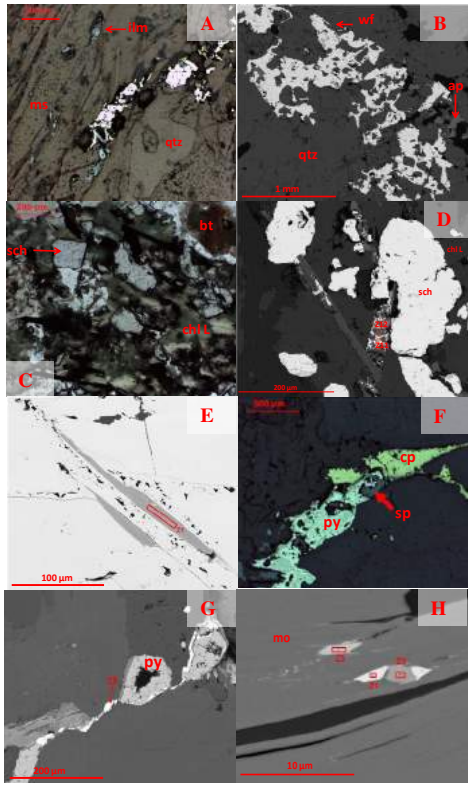

FIGURE 5.
A. MICROPHOTOGRAPH IN REFLECTED LIGHT OF MUSCOVITE (MS) ± QUARTZ (QTZ) ± ILMENITE (ILM). B. BSE IMAGE OF A DISSEMINATED FINE WOLFRAMITE (WF) ASSOCIATED WITH QUARTZ (QTZ) AND APATITE (AP). C. MICROPHOTOGRAPH IN TRANSMITTED LIGHT SHOWING THE RELATIONSHIP BETWEEN LAMELLAR CHLORITE (CHL L), BIOTITE (BT), SCHEELITE (SCH) AND SULPHIDES. D. BSE IMAGE OF SCHEELITE (SCH) AND WOLFRAMITE (Z11) REPLACING PRIOR ILMENITE (Z12). E. BSE IMAGE OF NB-W OXIDE (Z1) IN FRACTURES FROM WOLFRAMITE F. MICROPHOTOGRAPH IN REFLECTED LIGHT SHOWING THE RELATIONSHIP BETWEEN PYRITE (PY), CHALCOPYRITE (CP) AND SPHALERITE (SP). G. BSE IMAGE OF A SECOND GENERATION OF CASSITERITE (Z8) SURROUNDING PYRITE (PY). H. BES IMAGE OF VERY FINE BISMUTINITE (Z1), AG-TE SULPHIDES (Z2) AND GALENA (Z3) AS INCLUSIONS IN THE MOLYBDENITE (MO).

CONCLUSIONS

This study allowed identifying four stages of mineralization in the Santa Helena breccia: (I) ilmenite ± cassiterite I ± Th-U-REE phosphates ± muscovite; (II) wolframite ± scheelite ± Nb-W oxides; (III) sulphides of base metals (pyrite, chalcopyrite and sphalerite), cassiterite II and molybdenite; (IV) minor stannite, matildite, greenockite, bismutinite, native bismuth, galena and Ag-Te sulphides. In the quartz veins exploited in underground mine the stage I it was not identified and stage III is very well represented. The breccia pipe corresponds to a disseminated type of tungsten mineralization, representing a new mineralization type in Iberian Tin-Tungsten Variscan Province susceptible of exploitation in open pit and consequently representing potential for to support a new mine.

ACKNOWLEDGEMENTS

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Return

Rare-metal mineralization associated with a Variscan breccia pipe (Borralha, N Portugal)

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Borralha deposit is located at the Northwest of the Iberian Variscan Belt. In Borralha were exploited quartz veins with wolframite and scheelite. After Panasqueira, it was the second tungsten mine of Portugal. In addition to the mineralized veins, Borralha has the specificity to have two breccia pipes where the Santa Helena breccia (SHB) is the most important. In the European Variscan Belt, it is rare the occurrence of W mineralization in breccia pipes. SHB corresponds to a sub-vertical structure, with N-S major axis, cutting the contact between synorogenic Variscan granites and metasedimentary rocks (Silurian in age). In this contribution, we present some new data about the mineralization features in SHB based on the study of new drill-core samples. The ore occurs disseminated in the breccia elements, in the quartz cement and in late fractures. In the mineral assemblage, we can distinguish two main stages of deposition in a quartz-sericite-chlorite matrix: an oxidic stage and a sulphidic stage + native Bi. The oxidic stage is mainly characterised by the occurrence of wolframite and scheelite; the sulphidic stage is less expressive. We distinguish two generations of wolframite: wolframite I occurs in well-developed anhedral to subhedral crystals (≈500 µm) with MnO ranging from 2 to 11%, and wolframite II occurs in small euhedral crystals (≈10 µm) in late fractures cutting wolframite I and is characterised by an enrichment in MnO (>12% MnO). Wolframite I occurs associated with scheelite (≈200 µm) and also contains very fine crystals (5-20 µm) of niobium-tungstate, columbo-tantalite, monazite and fluorite. This mineral phases exhibit a complex internal texture characterised by a compositional zoning at the micrometer scale, resulting from successive episodes of crystallization caused by fluid circulation. The breccia pipe with rare-metal mineralization suggests a magmatic-hydrothermal history related with a intrusion still unknown at depth.

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Return

Rare-metal mineralization associated with Borralha breccia pipe (Northern Portugal)

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ABSTRACT

The Borralha deposit (Northern Portugal) was exploited for W and Cu, during the twentieth century (1902-1985), mainly from hydrothermal quartz veins with wolframite, scheelite and sulphides. In addition to the veins, Borralha has the specify to have two breccia pipes Venise and Santa Helena (SHB), where the second one is the biggest and the most important. SHB is mineralized and in this contribution are presented new data about the mineralization features based on the study of new drill core samples. The mineralization consists on fine wolframite and scheelite disseminated in the breccia elements, in the "cement" and also in late fractures. The occurrence of rare metal mineralization W (Sn, Nb, Ta, REE) in the breccia suggests a magmatic-hydrothermal history related with a still unknown source at depth.

I. Introdution

A large number of W deposits and occurrences are present in the Northwest of the Iberian Variscan Belt. In Portugal, the prevailing W and W (Sn) lode deposits are distributed through the Central Iberian Zone (CIZ) and Galícia Trás-os-Montes Zone (GTMZ), forming the "Iberian W-Sn Metallogenic Province" [1], included in the "Northern Metallogenic Province" [2] characterized by the presence of various W, W-Sn, W-Mo and Sn deposits occurring where Variscan granites intrude marine series, with ages ranging from Precambrian to Devonian.

II. Geology and Mineralogy

Borralha W deposit is located in the boundary between the CIZ and GTMZ [Figure 1A]. The dominant rocks types outcropping in this area are Silurian metamorphic rocks and Variscan granites [Figure 1B].

II.1. Santa Helena breccia (SHB)

The Santa Helena Breccia pipe corresponds to an outcropping sub-vertical N-S structure cutting the NW-SE contact between the porphyritic biotite granite (syn-D_3 Borralha granite), metasedimentary rocks and a zone characterized by an association of Borralha granite with big panels of metasedimentary rocks, the "Mixture zone" [3] [Figure 1C]. The contacts of the breccia are marked by N-S faults filled with massive barren quartz. Detailed underground, surface geological mapping and recent drilling indicate that it may be at least 575 m in length, over 150 m in width and 200 m in depth (known in -110 level). The elements of the breccia are mainly angular and their sizes are very variable (ranging from centimetres to metres) with similar lithological composition to the surrounding regional rocks (e.g. granites, tonalites, pegmatites, aplites and micashists) [Figure 1D]. This breccia is interpreted as a collapse breccia (Noronha,1979).

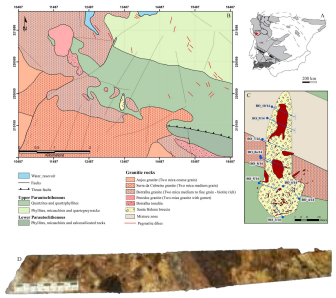

Figure 1 A. Iberian Variscan lithostratigraphic units: GTMZ, Galícia Trás-os-Montes Zone; CIZ, Central Iberian Zone; OMZ, Ossa Morena Zone; SPZ, South Portuguese Zone: a red star locates the Borralha area. B. Simplified geology map of Borralha area based on 1/50 000 scale regional geological maps using coordinate system ETRS-1989-Portugal-TM06. C. Simplified geology map of Santa Helena breccia. D. Representative sample of the SHB.

II.1.1. Occurrence of the ore minerals

- Disseminated fine (<1 mm) and very fine wolframite and scheelite associated with altered granitic elements;
- Disseminated medium (> 5 to 10 mm) to coarse (>10 mm) wolframite associated with quartz II;
- Coarse (< 10 mm) wolframite crystals in late quartz veins cutting the breccia elements [4].

II.1.2. Mineralogy of SHB

Petrographic studies, previously allowed to identify four mineralization stages [4-7]:

- **Stage I** - ilmenite ± cassiterite I ± apatite ± REE phosphates ± muscovite I ± scheelite I ± Fe, Mn chlorite ± biotite ± quartz I;
- **Stage II** - wolframite (I and II) ± scheelite II ± Nb-W oxides ± muscovite II ± Fe chlorite ± quartz II;
- **Stage III** - cassiterite II ± major sulphides (pyrite ± chalcopyrite ± sphalerite) ± Mg, Fe chlorite;
- **Stage IV** - native bismuth ± minor sulphides (molybdenite ± bismutinite ± galena ± matildite ± aikinite ± pavonite ± stannite ± greenockite) ± Fe, Mg chlorite ± quartz III.

III. Materials and Methods

During 2013 and 2014, trenches, channels and 9 drills were carried out on SHB by "Blackheath & Minerália" consortium. New representative samples were collected and several analytical techniques were used:

A. Optical Microscopy;
B. Scanning Electron Microscopy with Semi-quantitative Elementary Analyses (SEM-EDS);
C. Electron Microprobe analysis (EMPA)

IV. Results

Petrographic and SEM-EDS observations allowed to describe and characterize two different generations of wolframite (W I and W II) and scheelite (Sch I and Sch II).

- Sch I occur in euhedral crystals (>500 µm) associated with a Fe, Mn chlorite [Figure 2A] and the Sch II (≈500 µm) occur replacing the first generation of wolframite [Figure 2B].
- W I occurs as well-developed subhedral crystals (≈500 µm) and the wolframite II, only observed in SEM-EDS, as small euhedral crystals (≈10 µm) in late fractures cutting wolframite I [Figure 2C].
- Associated with wolframite I we can find small crystals (5 to 20 µm) of a niobium-tungstate, columbo-tantalite, monazite and fluorite [Figure 2D,E,F].

Electron Microprobe analyses were performed in wolframite, scheelite and niobium-tungstate [Table 1].

- The W I presents a MnO average content 5.74%, and W II is characterised by an enrichment in MnO (14.495%), consequently, a composition more huebneritic.
- The two generations of scheelite exhibit similar composition, however, Sch I presents some MnO (0.065%) and Sch II some FeO (0.118%). In any generation of scheelite is possible to find MoO_3.
- The niobium-tungstate exhibits a complex geochemical composition where the most important oxides are: Nb_2O_5 (56.846%), WO_3 (13.72%), MnO (12.045%), FeO (8.153%), TiO_2 (3.753%) and Ta_2O_5 (3.527%).
- The oxides exhibit a complex internal texture characterized by a zoning at the micrometre scale, resulting from the multiple episodes of crystallization and the ratio Nb/Ta≈13.77% can allowed a magmatic source for these mineral phases [8].

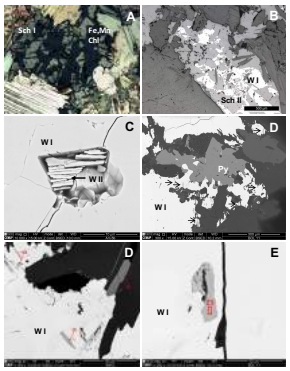

Figure 2 Rare-metal mineralization in the Santa Helena Breccia pipe. A. Microphotograph in reflected light of sub-euhedral crystals of scheelite I (Sch I) associated with a Fe, Mn chlorite (Fe,Mn Chl). B. Back-scattered electron (BSE) image of the scheelite II (Sch II) replacing wolframite I (W I). C. BSE image showing wolframite II (W II) infilling late fractures in W I. D. BSE image showing the association between W I and very fine crystals of niobium-tungstate (→). E. BSE image displaying the occurrence of niobium-tungstate phase (Z6≈100 µm) as inclusions in W I. F. BSE image showing very fine columbo-tantalite (Z3≈20 µm) as inclusion in W I.

EMPA results

Elements	Scheelite I	Scheelite II	Wolframite I	Wolframite II	Niobium-tungstate
Al_2O_3	-	-	-	-	0.011
FeO	-	0.118	17.03	9.7	8.153
CaO	18.85	19.19	0.059	0.07	0.039
MgO	-	-	-	-	0.094
TiO_2	-	-	-	-	3.753
MnO	0.065		5.74	14.495	12.045
P_2O_5	-	-	-	-	0.028
BaO	-	-	-	-	0.048
Nb_2O_5	-	-	0.055	0.054	56.846
SnO_2	-	-	-	-	0.971
Ta_2O_5	-	-	0.515	0.213	3.527
V_2O_5	-	-	-	-	0.019
WO_3	80.91	79.9	75.8	75.29	13.720
PbO	-	-	-	-	0.034
ZnO	-	-	-	-	0.028
NiO	-	-	-	-	0.015
Sc_2O_3	0.036	-	0.037	0.018	-
ZrO_2	-	-	-	-	0.372
SO_3	-	-	-	-	0.073
TOTAL	99.861	99.208	99.236	99.84	99.776

V. Conclusions

The described mineral assemblages and their dispersed mode of occurrence in a breccia with big volume (22.5 Mt) correspond to a new tungsten mineralization type in the Iberian Peninsula. The breccia pipe represents late-Variscan W (Sn, Nb, Ta, REE) mineralization suggesting a magmatic-hydrothermal history related with a magmatic intrusion still unknown at depth.

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Acknowledgments

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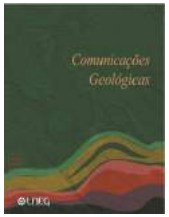
The Santa Helena Breccia Pipe (Borralha – North Portugal). A new type of W ore deposit in the Iberian Tin-Tungsten Metallogenic Province



Brecha de Santa Helena (Borralha – N Portugal). Um novo tipo de jazigo de tungsténio na Província Metalogénica Estano-Tungstífera Ibérica

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Abstract: The Borralha tungsten mine was exploited during the twentieth century mainly from vertical and sub-horizontal quartz veins enriched in wolframite, scheelite and sulphides. In addition to the vein structures, also occur two breccia pipes: Santa Helena (SHB) and Venise. The present work aims to contribute to the study of SHB. There are several hydrothermal alterations with variable intensity, mainly occurring near the contact between breccia fragments and the cement, and in late fractures: the alterations are mainly characterized by two muscovite generations, quartz and four chlorite generations. This study allowed identifying four stages of mineralization: Stage I (Ti–Sn-W-REE), Stage II (W ± Nb-Ta), Stage III (Fe-Cu-Zn ± Mo ± Sn) and Stage IV (Bi ± Pb ± Ag). The occurrence of disseminated mineralization in breccia pipes with a large volume correspond to a new tungsten deposit type in the Iberian Tin-Tungsten Metallogenic Province.

Keywords: Borralha, breccia pipe, tungstates, hydrothermal alteration, mineralization stages.

Resumo: O jazigo de tungsténio da Borralha foi explorado durante o século XX, em lavra subterrânea, foram explorados filões de quartzo verticais e sub-horizontais mineralizados em volframite, scheelite e sulfuretos. Além das estruturas filonianas, ocorrem, também, dois "pipes" brechóides mineralizados: brecha de Santa Helena (BSH) e brecha Venise. O presente trabalho tem como objetivo principal contribuir para o estudo da BSH. É possível observar diversas alterações hidrotermais com intensidade variável no contacto entre os elementos da brecha com o cimento e em fraturas tardias. Estas alterações são caraterizadas pela ocorrência de duas gerações de moscovite, quartzo e quatro gerações de clorite. Este estudo permitiu identificar quatro estádios de mineralização: Estádio I (Ti-Sn-W-REE), Estádio II (W±Nb-Ta), Estádio III (Fe-Cu-Zn ± Mo ± Sn) e Estádio IV (Bi ± Pb ± Ag). A ocorrência de mineralização disseminada em brechas de grande volume corresponde a um novo tipo de depósito de tungsténio na Província Metalogénica de Estano-Tungstífera Ibérica.

Palavras-chave: Borralha, "pipe" bréchico, tungstatos, alterações hidrotermais, estádios de mineralização.

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1. Introdution

Hydrothermal ore deposits are big geochemical anomalies in the Earth that provide us the clearest evidence of the past flow of solutions through faults, fractures and porous rocks that, in the process, dissolved, transported and concentrated elements of economic interest (Wilkinson, 2001). In Portugal, the prevailing W and Sn lode deposits are distributed all through the Central Iberian Zone - CIZ and Galiza Trás-os-Montes Zone - GTMZ (Julivert *et al*., 1975; Ribeiro, 2006), forming the so-called "Iberian Sn-W Metallogenic Province" (Neiva, 1944), included in the "Northern Mineralogenic Province" (Thadeu, 1965) characterized by the presence of various W, W-Sn, W-Mo and Sn ore-systems. The distribution of occurrences of W and Sn in the North of Portugal shows an occurrence according to alignments parallel to Variscan structures (*e.g*. Neiva, 1944; Noronha *et al*., 2006). These systems occur where Variscan granites intrude marine series, with ages ranging from Precambrian to Silurian-Devonian (*e.g*. Neiva, 1944; Thadeu, 1965, 1977). It seems that the binary granite-metasedimentary rock is essential to the development of these ore deposits. Furthermore, granites can act as an important source of metals and/or source of heat needed to sustain the hydrothermal systems for a significant time range. This heat flow regime supported an extensive hydrothermal activity throughout the entire crust, involving distinct fluid sources in successively lower P-T conditions along a continuum that provided long-lived systems, some of them comprising significant amounts of ore mineral phases, namely wolframite, cassiterite and sulphides (Mateus and Noronha, 2010).

Borralha, until its closure in 1985, was the second largest tungsten mine in Portugal after Panasqueira. At Borralha the deeper underground works were at level -210 (Level 0, level of the Borralha river, is at a height of 770 m) exploiting vertical quartz veins (more than 45º dip) and sub-horizontal veins (<30º dip). The ore was composed by wolframite and scheelite associated with minor minerals like chalcopyrite and molybdenite and other accessory minerals pyrite, pyrrhotite, sphalerite, bismuthinite, marcasite, galena, native bismuth and Pb-Bi-Ag sulphosalts. The total production of wolframite (82%) and scheelite (18%) concentrates (65% WO_3), from 1904 to 1985, was estimated at about 18500 t (Noronha, 1983).

Borralha has the particularity to have, in addition to the vein structures, two breccia pipes: Santa Helena breccia (SHB) and Venise breccia. This fact is rare, because in the European Variscan belt only one more example is known at Puy les Vignes in the French Massif Central (Cuney *et al*., 2002; Harlaux *et al*., 2015a, b).

SHB, was named as "stockwerk", is the only one outcropping and has been partially mined, in open pits in 50's of the last century, because it has tungsten mineralization in ore shoots ("ore pockets"). A drilling exploration program started on April 2014, performed by the consortium Blackheath and Minerália being carried out 9 drills that contributing to the study of SHB. This work presents, the results of geological, mineralogical and geochemical studies for definition and identification of the mineralization types in SHB.

2. Geological setting

Borralha area (Montalegre) is located at the Northwest of the Iberian Peninsula in the boundary between the CIZ (autochthonous terranes, Ribeiro *et al*., 1990, Ribeiro, 2006) and GTMZ (parautochthonous terranes) (Fig. 1A). The dominant host rocks are Silurian metamorphic rocks and granites (Noronha and Ribeiro, 1983; Ribeiro *et al*., 2001). Different types of synorogenic Variscan granitoids can be identify: syn-D3 granitoids (Borralha tonalite and Borralha granite, syn-D3 granites (Serra da Cabreira and Ruivães) and post-D3 granite (Penedos) (Noronha and Ribeiro, 1983; Ferreira *et al*., 1987) (Fig. 1B).

2.1. Santa Helena breccia

The Santa Helena Breccia (SHB) corresponds to a sub-vertical N-S structure cutting the contact between syn-D3 granitoids (Borralha), metasedimentary rocks (Silurian in age) and a "Mixture zone" characterized by granites including big panels of metasedimentary rocks (Noronha, 1983) (Fig. 1C). The E and W limits of the breccia are marked by extremely fractured limits with huge barren N-S quartz veins. Detailed historical underground, surface geological mapping and recent drilling of SHB indicate it is at least 575 m in length, over 150 m in width and 200 m in height (known till -110 level). The major axis has a strike close to N-S. The fragments of the breccia are mainly angular, and their sizes are very variable, and it is possible to find side by side metric blocks next to centimetric blocks. The lithological composition of the fragments is identical to the surrounding rocks, *e.g*., granite, tonalite and metasedimentary rocks. The breccia has been interpreted as a collapse breccia pipe by Noronha (1979). Hydrothermal alterations are visible, mainly near the contact breccia fragments-cement and in late fractures. These alterations occur with variable intensity in apparently unaltered fragments and are characterized by the occurrence of muscovite I and II, quartz and four generations of chlorite (Gonçalves and Noronha, 2017). It is more evident when the fragments are of granite, pegmatite or aplite where K-feldspar and plagioclase are partially replaced by quartz II + muscovite II and biotite by chlorite.

The mineralization is characterized by the association of W, Cu, Zn, Mo and minor Nb, Sn, Th, U, REE, Bi, Ag, Pb. In general, wolframite is fine-grained and occurs disseminated in the fragments and/or associated with other minerals, in zones with obvious hydrothermal alterations. However, the existence of late veinlets, with clear quartz and coarse-grained wolframite cutting the breccia, is recognizable and it must be remembered that the first exploitations of SHB in upper levels occurred in pockets exploited in open pits.

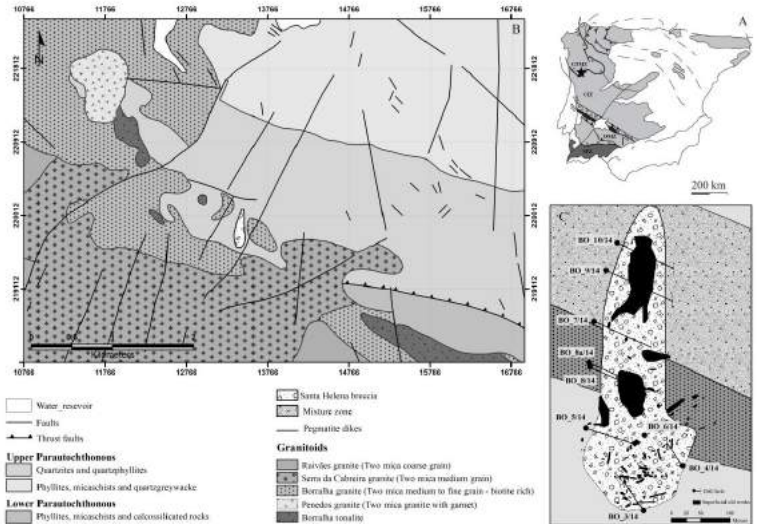

Figure 1. Iberian Variscan lithostratigraphic units (after Ribeiro & Sanderson, 1996 in Onézime et al., 2003): GTMZ, Galicia Trás-os-Montes Zone; CIZ, Central Iberian Zone; OMZ, Ossa Morena Zone; SPZ, South Portuguese Zone: a star locates the Borralha area. B. Simplified geology of Borralha area based on 1/50000 scale geological maps (6A - Montalegre (Noronha & Ribeiro, 1983), 6C - Cabeceiras de Basto (Ribeiro et al., 2001)), using coordinate system ETRS_1989_Portugal_TM06. C. Simplified geology of Santa Helena breccia (blackheath resources, accessed in 9/january/2018).

Figura 1. Unidades litoestratigráficas da Península Ibérica Varisca (depois de Ribeiro & Sanderson, 1996 in Onézime et al., 2003): ZGTM, Zona Galiza Trás-os-Montes; ZCI, Zona Centro Ibérica; ZOM, Zona Ossa Morena; ZSP, Zona Sul Portuguesa: a estrela indica a localização da área da Borralha. B. Mapa geológico simplificado da área da Borralha baseado nos mapas geológicos à escala 1/50000 (6A - Montalegre (Noronha & Ribeiro, 1983), 6C - Cabeceiras de Basto (Ribeiro et al., 2001)), o sistema de coordenadas utilizado foi ETRS_1989_Portugal_TM06. C. Mapa geológico simplificado da brecha de Santa Helena (blackheath resources, acedido em 9/janeiro/2018).

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3. Materials and Methods

For this study, two drill cores were selected, BO_5/14 and BO_8a/14 (see Fig. 1C), because they were considered more representative of the breccia. Twenty-five samples were collected from the drill cores and thirty polished thin-sections were made. Several analytical techniques were used in this study: optical microscopy, Scanning Electron Microscopy with semi-quantitative elementary analyses (SEM-EDS) and geochemical analyses. Petrographic observations of polished thin-sections were performed at the Faculty of Sciences, University of Porto, using a stereomicroscope Zeiss Stemi SV11 Apo coupled with a Sony Cyber-Shot DSC-S75 digital camera and also using a Leica DM LSP polarizing microscope with transmitted and reflected light, coupled with a Leica camera with LAS EZ software 2.0.0. SEM-EDS analyses were performed at the Materials Centre of the University of Porto using an FEI Quanta 400 FEG-ESEM/EDAX Genesis X4M instrument. The SEM was operated at 15 kV in high-vacuum mode, manual aperture, and 4.5 beam spot sizes. The geochemical analyses were carried out by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by the accredited commercial laboratories of the ALS Group at Seville (Spain).

4. Results

4.1. Lithological description and Tungsten grades

The drilling carried out at SHB were extremely important, because it allowed the recognition of the structure in depth. Distinct rocks types were found constituting the breccia fragments, which were always similar to the regional host rocks. Breccia fragments can appear in big blocks (metric size) and, in this case, it is difficult to recognize the breccia features. On the other hand, the breccia s.r. is well identified, in the cores, when the fragments are centimetric and angular with mineralized cement (Fig. 2). There are several types of quartz in the cement: a milky massif quartz (quartz I), with no obvious mineralization, a clearer one (quartz II) with a greyish colour associated with mineralization and a late hyaline quartz (quartz III). It is also visible a random but consistent muscovite I and II (muscovite II can be designated as sericite) disseminated in the fragments or massive in late quartz veins.

In Figure 3A it is possible to observe a pictorial log from Santa Helena breccia. The geochemical values from the samples collected in the cores combined with the different occurring lithologies allowed to visualize the mode of distribution of tungsten contents (Fig. 3B). The more significant contents (275 to 17600 ppm of W) occur from the 106 to 176 m corresponding to domains of breccia with some oxidation, boxworks and medium-grained wolframite (Table 1).

Figure 2. Representative sample of Santa Helena breccia where is possible to observe angular fragments with distinct composition.

Figura 2. Amostra representativa da brecha de Santa Helena onde é possível observar fragmentos angulosos de composição litológica distinta.

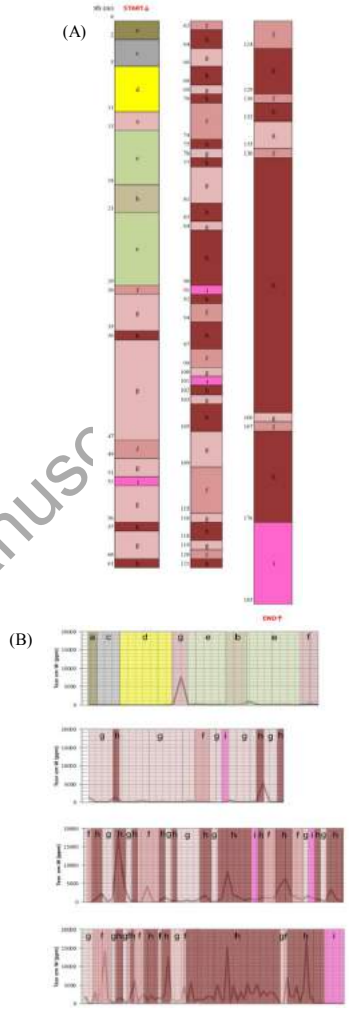

Figure 3. A. Pictorial log from BO_8a/14 drill core in Santa Helena breccia: a – gauged tonalitic granite; b – breccia more tonalitic; c – gauged tonalitic granite with a quartz vein level; d – quartz vein from W limit; e – very fractured breccia more schist with some oxidation; f - gauged level of the breccia; g – fractured breccia with oxidation; h –breccia fractured with some oxidation and boxworks with medium-grained wolframite; i – granitic breccia with some sulphides, some oxidation and sometime gauged. B. Distribution in depth of the tungsten contents and their relationship with th different types of lithologies; a-i – see previously mentioned description.

Figura 3. A. Pictograma da sondagem BO_8a/14 da brecha de Santa Helena: a – granit tonalítico alterado; b- brecha tonalítica; c – granito tonalítico alterado com filão d quartzo; d – filão de quartzo do limite W; e – brecha muito fraturada com xisto presença de oxidação; f – nível de brecha alterada; g – brecha fraturada com oxidação h – brecha fraturada com oxidada com boxworks e volframite de granulometria médi i – brecha granítica oxidada com sulfuretos. B. Distribuição dos teores de volfrâmio er profundidade e a relação com as diferentes litologias: a-i – ver descrição anteriorment mencionada.

Table 1. Tungsten contents (ppm) in the lithologies presented in the Santa Helena breccia.

Tabela 1 Teores de tungsténio (ppm) das litologias presentes na brecha de Santa Helena.

Lithology	Minimum	Maximum	Mean	Standard Deviation
Gauged tonalitic granite	92	120	106	20
Gauged tonalitic granite with a quartz vein level	31	56	40	14
Quartz vein from W limit	1	41	15	14
Breccia more tonalitic	40	283	130	133
Very fractured breccia more schist with some oxidation	91	904	222	213
Fractured breccia with oxidation	19	6290	722	1543
Gauged level of the breccia	18	14200	1690	3131
Mixed breccia fractured with some oxidation and boxworks with medium-grained wolframite	275	17600	2878	3553
Granitic breccia with some sulphides, chlorite, some oxidation and sometimes gauged	8	897	151	281

4.2. Occurrence of the tungsten minerals in the drill cores

The macroscopic study of the samples allowed observing different types of occurrence of the tungsten mineralization. It was possible to identify the presence of wolframite and scheelite, where the first one is more abundant. Different types of disseminated tungstates were identified: (i) fine to very fine-grained wolframite and scheelite, in the fragments (Fig. 4A), (ii) medium (> 5 to 10 mm) to coarse-grained (> 10 mm) wolframite in the cement (Fig. 4B), in both cases associated with muscovite I and II ± quartz ± Fe chlorite and (iii) coarse-grained (> 10 mm) wolframite in late quartz veins cutting the breccia (Fig. 4C). The sulphides occur associated with Mg, Fe chlorite (Bobos and Noronha, 2017).

Figure 4. Types of occurrence of the W mineralization in the Santa Helena breccia. A. Fine to very fine-grained wolframite and scheelite, in the fragments. B. Medium (> 5 to 10 mm) to coarse-grained (> 10 mm) wolframite in the cement. C. Coarse-grained (> 10 mm) wolframite in late quartz veins cutting the breccia.

Figura 4. Modo de ocorrência da mineralização na brecha de Santa Helena. A. Volframite fina a muito fina (minerais máficos de granulometria muito fina) e scheelite disseminadas nos elementos. B. Volframite de granulometria média a grosseira (> 5 a 10 mm) associada a ao cimento. C. Volframite grosseira (> 10 mm) associada a filões de quartzo tardios que cortam a brecha

4.3. Petrography

The petrographic study of the selected samples made possible to observe some mineralogical features of SHB. It must be emphasized that in the present study only the dispersed mineralization was studied because is typical of the breccia. The new petrographic observations led to the definition of four mineralization stages: Stage I (Ti–Sn-W- REE), Stage II (W ± Nb-Ta), Stage III (Fe-Cu-Zn ± Mo ± Sn) and Stage IV (Bi ± Pb ± Ag).

4.3.1. Stage I (Ti-Sn- W-REE)

The crystals of quartz occur in anhedral to subhedral grains and varying dimensions (500 µm to 1mm), associated with this quartz occurs muscovite I and II. The first generation of muscovite (ms I) is represented by well-developed crystals (>500 µm) and the second one (ms II, known as sericite) is characterized by small crystals (<100 µm) clustered with a preferential oriented distribution. It was also possible to identify ilmenite (200 to 500 µm) superimposed on the quartz and muscovite I (Fig. 5A), indicating a latter crystallization of these silicates. Small crystals of cassiterite (cst I, <50 µm) also occur associated with muscovite I. Biotite (200 to 400 µm) sometimes replaced by chlorite, apatite (>400 µm) with inclusions of monazite, zircon and U, Th, Y, REE phosphates (<20 µm) also occurs in this stage (Fig. 5B). A first generation of scheelite (Sch I) is also present in this stage, occurring in sub-euhedral well-developed crystals (≈500 µm) associated with Fe, Mn chlorite in a muscovite I and II + quartz cement (Fig. 5C).

4.3.2. Stage II (W±Nb-Ta)

This stage can be characterised by the occurrence of wolframite I and II, scheelite II and mineral phases enriched in Nb-Ta. Wolframite I present several modes of occurrence: (i) dispersed in muscovite II ± quartz cement ± Fe chlorite, suggesting a crystallization in the void spaces (<500 µm) and including cassiterite I (Fig. 5D); (ii) in very fine-grained crystals (<20 µm) replacing ilmenite (Fig. 5E); and (iii) in medium to coarse-grained crystals (>2 mm). In wolframite I it is possible to observe fine inclusions (≈ 5-20 µm) of niobium-tungstate oxides, columbo-tantalite (coltan), monazite and fluorine (Fig. 5F,G). Sporadically it is possible to distinguish a second generation of wolframite (w II) occurring in small zoned euhedral crystals (≈ 10 µm) filling late fractures and/or cavities in wolframite I (Fig. 5H). Associated with wolframite I can occur a second generation of scheelite (Sch II ≈200 µm) in anhedral crystals (≈ 200 µm) (Fig. 5I).

4.3.3. Stage III (Fe-Cu-Zn ± Mo ± Sn)

At this stage, it was possible to observe the contemporaneousness between the main sulphides of pyrite (Py, 200 to 400 µm), chalcopyrite (Cc, >500 µm), sphalerite (Sp, ≈500 µm) (Fig. 5J), Mg, Fe chlorite and adularia. The main sulphides occur associated with pre-existing muscovite I and II ± quartz and, it is possible to identify rare small crystals of molybdenite (<100 µm). A second generation of cassiterite (50 to 100 µm) occurs filling latter fractures (Fig. 5K).

4.3.4. Stage IV (Bi ± Pb ± Ag)

In this stage was possible to identify some scarce and fine-grained occurrences of native bismuth, galena and Bi-Te-Ag sulphosalts. The Bi-Te-Ag sulphosalts fill fractures or voids in major sulphides, from stage III, the identification of these fine

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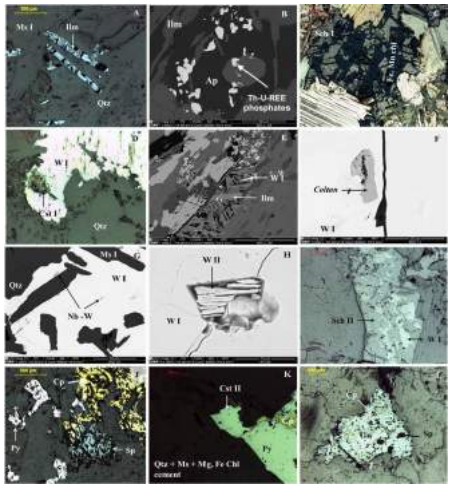

Figure 5. A) Microphotograph in reflected polarized light of ilmenite (ilm, >500 µm) associated with quartz (Qtz) ± muscovite I (Ms I). B) Backscattered electron (BSE) image showing the occurrence of fine Th-U-REE phosphates (≈10 µm) as inclusions partially elongated and parallel to the apatite b axis. C) Microphotograph in transmitted light of scheelite I (Sch I, ≈500 µm) associated with Fe, Mn chlorite (Fe, Mn Chl, ≈500 µm) in a quartz ± coarse muscovite (>500 µm) matrix. D) Microphotograph in reflected polarized showing the association between wolframite I (W I, >500 µm) and cassiterite I (Cst I, ≈200 µm), the last one crystallized in the end of stage I. E) BSE image showing a replacing of ilmenite by wolframite I. F) BSE image showing very fine columbo-tantalite (Coltan ≈20 µm) as inclusion in W I. G) BSE image of wolframite I (> 100 µm) with fine inclusions of Nb-W oxides (≈20 µm) randomly scattered showing a preferential orientation. H) BSE image of layered wolframite II (W II, ≈20-30 µm) filling cavities in wolframite I. I) Microphotograph in reflected polarized light of scheelite II (Sch II, ≈200 µm) associated with wolframite I (≈200 µm) in a quartz (Qtz) ± coarse muscovite (Ms I ≈ 500 µm) matrix. J) Microphotograph in reflected polarized light showing the relationship between pyrite (Py, ≈500 µm)), chalcopyrite (Cp, >500 µm)) and sphalerite (Sp, ≈500 µm). K) Microphotograph in reflected polarized light of second generation of cassiterite (Cst II, ≈200 µm) crystallized in the rim of the major sulphides (pyrite – Py, >500 µm and chalcopyrite - Cp, ≈ 100 µm). L) Microphotograph in reflected polarized light showing a mineral phase of galena (Gn, >500 µm) with inclusions of chalcopyrite and sphalerite. The abbreviations used to identify the different mineral phases followed the symbols proposed by Cache (1956) and Kretz (1983).

Figura 5. A) Microfotografia em luz refletida polarizada onde é possível verificar a associação da ilmenite (ilm, >500 µm) com uma matriz composta por quartzo (Qtz) ± moscovite (Ms I). B) Imagem em eletrões retrodifundidos (ER) mostrando a ocorrência de fosfatos de Th-U-Terras Raras (≈10 µm) como inclusões parcialmente alongadas e paralelas ao eixo b da apatite (≈50 µm). C) Microfotografia em luz transmitida mostrando a associação da scheelite I (Sch I, ≈10 µm) com a clorite de Fe, Mn (Fe, Mn Chl, ≈500 µm) numa matriz constituída por quartzo ± moscovite grosseira (>500 µm). D) Microfotografia em luz refletida mostrando a associação entre a volframite I (W I, >500 µm) e a cassiterite I (Cst I, ≈200 µm), sendo que esta última cristalizou no fim do estádio I. E) Imagem m ER mostrando a substituição da ilmenite pela volframite I. F) Imagem em ER mostrando columbo-tantalites de granulometria fina (Coltan ≈20 µm) como inclusões na W I. G) Imagem em ER da volframite I (>100 µm) com finas inclusões de óxidos de Nb-W (≈20 µm) dispersos segundo uma orientação preferencial. H) Imagem ER evidenciando a cristalização da volframite II (W II, ≈20-30 µm) em cavidades na volframite I. I) Microfotografia em luz polarizada refletida mostrando a scheelite II (Sch, ≈200 µm) associada à volframite I (≈200 µm) numa matriz de quartzo (Qtz) ± muscovite grosseira (Ms I, ≈500 µm). J) Microfotografia em luz polarizada refletida mostrando a relação existente entre a pirite (Py, ≈500 µm), calcopirite (Cp, >500 µm) e a esfalerite (Sp, ≈500 µm). K) Microfotografia em luz polarizada refletida da segunda geração de cassiterite (Cst II, ≈200 µm) cristalizada nos bordos de sulfuretos maiores (pirite – Py, >500 µm e calcopirite – Cp, ≈100 µm). L) Microfotografia em luz polarizada refletida mostrando um mineral de galena (Gn, >500 µm) com inclusões de calcopirite e esfalerite. As abreviações utilizadas para identificar as diferentes fases minerais seguem os símbolos propostos por Cache (1956) e Kretz (1983).

mineralization it was only possible using SEM. In Figure 5L it is possible to observe a coarse-grained of galena (<500 µm) with inclusions of chalcopyrite and several small inclusions of sphalerite (<100 µm). The deposition of latter generation of Fe, Mg chlorite is also recognized.

5. Discussion and Conclusions

Borralha has the particularity to have, in addition of the quartz veins, two breccia pipes (Noronha 1979, 1983). The quartz veins already exploited in underground mining were described in precedent studies. Now it was possible to observe and study the mineralization of the outcropping breccia, the Santa Helena breccia (SHB), in the sequence of a recent drilling program.

The study of SHB allowed to the definition and identification of successive stages of mineralization, different from that of the quartz veins exploited until 1985 in Borralha mine. The present study indicates independent periods of ore deposition for a disseminated fine to medium-grained mineralization present in the breccia pipe not found in the exploited quartz veins. The main differences consist in the presence of a stage I were scheelite occur associated with ilmenite, cassiterite and REE phosphates and a second stage with wolframite, scheelite and Nb-Ta oxides.

The already proved volume of the breccia, 22.5 Mt, above -60 level, and the disseminated tungsten mineralization implying interesting grades, are of particular interest, because they can make possible the exploitation in "open pit" of this new type of W ore deposit, a "Breccia pipe with disseminated W mineralization"

Acknowledgements

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The Santa Helena Breccia Pipe (Borralha). An example of occurrence of disseminated W mineralization.

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Abstract

The Borralha deposit was exploited during the last century, being one of the most important deposits of tungsten in Portugal. This occurrence was mainly exploited in vertical and sub-vertical veins with wolframite, scheelite and sulphide mineralization, adding to this structures occur two breccia bodies: **Santa Helena breccia (SHB)** and Venise breccia. The present work aims to contribute to the study of the SHB, an atypical Variscan tungsten deposit. Several mineral deposition stages were identified: stage I- ilmenite ± cassiterite I ± Th-U and REE phosphates ± scheelite I ± muscovite I ± chlorite I; stage II- wolframite I ± Nb-W oxides ± muscovite II ± chlorite II; stage III- pyrite ± chalcopyrite ± sphalerite ± cassiterite II; stage IV- wolframite II ± scheelite II ± (stannite, molybdenite, matildite, greenockite, native bismuth, galena and sulphosalts (Te, Ag)) ± chlorite III. There are several hydrothermal alterations with variable intensity, mainly occurring near the contact between elements-quartz element and, in late fractures. The defined stages are different from the previous defined for Borralha mineralized quartz veins and correspond to a disseminated mineralization representing a new mineralization type in the Iberian Tungsten Variscan Province.

Introduction

Allied with the study of metallic deposits of the Iberian Peninsula, we need always to consider the Variscan cycle. Geological processes related with this orogeny were the responsible for the mobilization and deposition of metallic elements, so that the hydrothermal tungsten mineralizations were conditioned by the Variscan structures as well as her alignments. In addition to that the tungsten deposits, usually, occur associated with the contact of granites with metasedimentary rocks and on the contact between granites with different ages [1].

Borralha area occurs in the contact between the Central Iberian Zone (autochthonous terranes) and the western part of Galiza-Trás-os-Montes zone (parauthocthonous terranes),

Santa Helena Breccia (SHB)

It is a body corresponding to a sub-vertical structure, with a N-S major axis with 575 m in length, over 150 m in width and at least 200 m in height (**Figure 1**). It is composed by mainly angular elements, with a large variety of sizes, from centimetric to metric. Having all this in mind, this breccia was interpreted as a collapse breccia [2,3]. The SHB cuts a NW-SE contact between a syntectonic biotite granite (Borralha granite) and metassedimentary rocks (Silurian in age), and its composition is identical to the surrounding rocks, i.e., granite, tonalite, pegmatite and schists. The elements that compose the breccia were subject to a hydrothermal alteration with a variable intensity, occurring mainly near the contact elements- quartz cement and in late fractures. It is characterized by a mineralization dispersed in the breccia "matrix" and in fractures cutting the breccia elements. The mineralization is characterized by the association of W, Cu, Zn, Mo and minor Nb, Sn, Th, U, REE, Bi, Ag, Pb.

SBH corresponds to an extraordinary example of a tungsten deposit in the Variscan orogeny.

Methods and Materials

The studied samples were obtained from a 10 drill cores campaign during 2014 made by the consortium Blackheath - Minerália.

From those were selected the drill core **Bo_5/14** and **Bo-8a/14** (**Figure 2**).

These samples were described macroscopically and after were studied with the recourse of several analytical technics such as:

- Optical microcopy;
- Scanning electronic microscopy (SEM-EDS);
- Geochemistry.

Results

Mineralization in the drilling cores

Macroscopically were identify fine wolframite and scheelite associated with quartz and muscovite in the "matrix" elements and medium to coarse wolframite associated with quartz **(Figure 3A)**. Were also identified several quartz veinlets associated with coarse wolframite crystals.(**Figure 3B**).

Mineralogy

Stage I- ilmenite ± cassiterite I ± Th-U and REE phosphates ± scheelite I ± muscovite I ± chlorite:

In this stage, it was observed that ilmenite (200- 500µm) is associated with quartz (500µm - 1 mm) and muscovite I (>500µm). In addition to that, it was also identified cassiterite I (<50µm) contained inside of wolframite I crystals (**Figure 4A**). This stage, is also characterized by the presence of biotite and phosphates, such as, apatite and monazite with fine inclusions of REE. Scheelite I (≈200µm) is rare, occurring mostly contained in wolframite I (<500µm)(**Figure 4B**).

Stage II- wolframite I ± Nb-W oxides ± muscovite II ± chlorite:

The stage II is characterized by the presence of wolframite associated with quartz and muscovite II (<100µm). This wolframite I, sometimes, occurs replacing crystals of ilmenite (**Figure 4C**) . Adding to that, it also occurs fine crystals of Nb-W oxides associated with tungstates and chlorite II (**Figure 4D**) .

Stage III- main sulphides (pyrite, chalcopyrite, sphalerite) and cassiterite II ± chlorite:

The main sulphide deposition is characterized by pyrite (200-400µm), chalcopyrite (>500µm) and sphalerite (≈ 500µm) all contemporary (**Figure 4E**). It is also observed a second generation of cassiterite II (50-100µm).

Stage IV- wolframite II ± scheelite II ± (stannite, molybdenite, bismutinite, matildite, native bismuth) ± galena and sulphosalts (Te, Ag).

In this stage was identified wolframite II (50µm), usually, with a more lamellar habit and enriched in Mn. Scheelite II (200µm) occurs manly in substitution of wolframite I (**Figure 4F**). Adding to that, were observed fine crystals of the mineral mention above in association with sulphides and chlorite.

Hydrothermal alterations

There are several hydrothermal alterations, mainly occurring near the contact breccia elements-quartz cement, and in late fractures, characterized, by muscovite ,by quartz ± muscovite II ± and different chlorite types.

A genetic linkage of wolframite and scheelite was found for Fe,Mn-chlorite, whereas the Fe,Mg–chlorite is linked with sulphide mineralization [4].

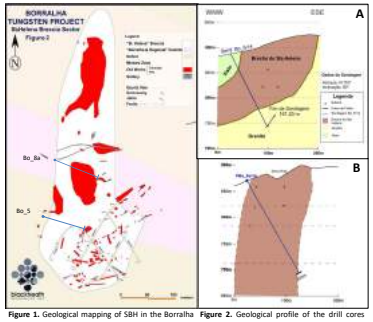

Figure 1. Geological mapping of SBH in the Borralha area. With the studied drill cores (Bo_5 and Bo_8a) **Figure 2.** Geological profile of the drill cores studied (Bo_5 and Bo_8a) in the SHB.

Figure 3. Occurrence of mineralizations in cores of SHB; **A)** Fine wolframite associated with greisenized granitic elements. **B)** Quartz veinlets associated with coarse wolframite.

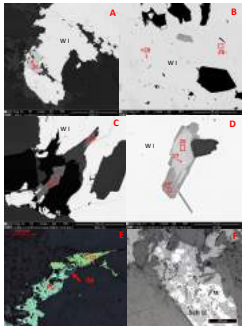

Figure 4. A) BSE image of the association of cassiterite I (Z6) with wolframite I (W I) crystals. **B)** BSE image of the relation of scheelite I (Z8) with the wolframite I (W I). **C)** BSE image of the presence of ilmenite (Z4) contained in wolframite I (W I) crystals. **D)** BSE image of the presence of the REE oxides (Z5 and Z6) and REE niobates, on a wolframite I (W I) crystal. **E)** microphotography of the relation of the main sulphides pyrite (Py), chalcopyrite (Ccp) and sphalerite (Sp). **F)** microphotography of the substitution of the crystals of wolframite I (w I) by the scheelite II (Sch II)

Conclusions

In this study were identified **four stages of mineralization:** stage I- ilmenite ± cassiterite I ± Th-U and REE phosphates ± scheelite I ± muscovite I ± Fe,Mn-chlorite; stage II- wolframite I ± Nb-W oxides ± muscovite II ± Fe,Mg-chlorite; stage III- pyrite ± chalcopyrite ± sphalerite ± cassiterite II; stage IV- wolframite II ± scheelite II ± (stannite, molybdenite, matildite, greenockite, native bismuth, galena and sulphosalts (Te, Ag)). The defined stages are different from the previous defined for quartz veins and correspond to a disseminated type of mineralization representing a new mineralization type in Iberian Tungsten Variscan Province.

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Return to Subjects

RARE EARTH ELEMENTS MOBILITY DURING HYDROTHERMAL ALTERATION: EVIDENCE FROM SANTA HELENA BRECCIA, BORRALHA AREA (NORTH PORTUGAL)

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ABSTRACT

The Borralha deposit (Northern Portugal) was exploited for W and Cu, during the twentieth century, mainly from hydrothermal quartz veins with wolframite, scheelite and sulphides. In addition to the vein structures, there also occur two breccia pipes: Santa Helena and Venise. This research pretends to understand the role of the hydrothermal alterations in the occurrence and distribution of the Rare Earth Elements (REE) of Santa Helena breccia (SHB). To achieve this goal, several methodologies were used to compare the mineralogy and geochemistry of the altered lithologies composing the SHB and the unaltered regional granites: optical microscopy, scanning electron microscopy (SEM-EDS) and geochemical analyses. Optical petrography and SEM-EDS performed in samples from the breccia allowed the identification of apatite, monazite and Th-U-REE phosphates as the main hosts for REE. Geochemical analyses performed on representative samples of breccia and regional granites showed an enrichment of REE in the breccia comparatively to the known regional granites. The results of this study show that REE can be considered mobile during the fluid-rock interaction (specifically in greisenization) related to magmatic-hydrothermal fluids, associated with a buried cupola of a late-orogenic granite, that implies a W, Ti, Sn, P, Th, U, REE mineralization.

Keywords: Rare Earth Elements, granites, Santa Helena breccia, Borralha W deposit

1. INTRODUTION

Hydrothermal ore deposits are great geochemical anomalies in the Earth that provide us the clearest evidence of the past flow of solutions through faults, fractures and porous rocks that, in the process, dissolved, transported and concentrated elements of economic interest (Wilkinson, 2001). In Portugal, the prevailing W and Sn lode deposits are distributed all through the Central Iberian Zone (CIZ) and Galicia Trás-os-Montes Zone (GTMZ) (Ribeiro et al., 1990) forming the so-called "Iberian Sn-W Metallogenic Province" (Neiva, 1944), included in the "Northern Metallogenic Province" (Thadeu, 1965) characterized by the presence of various W, W(Sn), W(Mo) and Sn ore-systems. These systems occur where Variscan granites intrude marine series, with ages ranging from Precambrian to Silurian-Devonian (e.g. Thadeu, 1977).

In the last century, Borralha was the second W mine in Portugal. The deeper underground works were at level -210 (Level 0, the river Borralha level, is at a height of 772 m) exploiting vertical quartz veins (more than 45º dip) and sub-horizontal quartz veins (less than 30º dip). Major ore minerals are wolframite and scheelite associated with minor ore minerals like chalcopyrite, molybdenite and other minerals such as quartz, pyrite, pyrrhotite, sphalerite, bismuthinite, marcasite, galena, native bismuth and Pb-Bi-Ag sulphosalts. The total production of wolframite and scheelite concentrates, from 1904 until the closing of Borralha, was estimated at about 18500 t (Noronha, 1983). Borralha deposit has the particularity to have, on addition to the vein structures, two breccia pipes with quartz cement: Santa Helena breccia (SHB) and Venise breccia. SHB is the only one outcropping and has been partially mined, near the surface during the 50s of the last century, because it has tungsten mineralization in its cement and in ore shoots ("ore pockets"), and it was named as "stockwork". In the European Variscan belt only one more example of breccia pipe was studied, Puy les Vignes in the French Massif Central (Cuney et al., 2002; Harlaux et al., 2015a,b).

2. GEOLOGICAL SETTING

Borralha area (Montalegre) is located at the Northwest of the Iberian Peninsula in the boundary between the CIZ (autochthonous terrane) and GTMZ (parautochthonous and allochthonous terranes) (Fig. 1A). The dominant rocks types outcropping in this area are Silurian metamorphic rocks and Variscan granites. It is possible to distinguish different types of synorogenic granites: a syn-D3 porphyritic biotite granite (Borralha granite) and two-mica peraluminous granites, the most abundant regional granites, and a post-D3 leucocratic granite (Penedos granite) considered as related to Gerês late-orogenic massif (Noronha & Ribeiro,1983) (Fig.1B).

2.1. SANTA HELENA BRECCIA (SHB)

SHB corresponds to an outcropping sub-vertical N-S structure cutting the NW-SE contact between the Borralha granite, metasedimentary rocks and a zone characterized by Borralha granite with big panels of metasedimentary rocks, known as the "Mixture zone" (Noronha, 1979) (Fig. 1C). The contacts of the breccia are marked by faults with massive barren quartz. Detailed underground, surface geological mapping and recent drilling in SHB indicate that it may be at least 575 m in length, over 150 m in width and 200 m in depth (known in -110 level). The elements of the breccia are mainly angular and their sizes are very variable. It is possible to find, side by side, metric blocks next to centimetric elements with similar lithological composition to the surrounding regional rocks, e.g., granites, tonalites, pegmatites, aplites and micaschists. This breccia was interpreted as a collapse breccia by Noronha (1979).

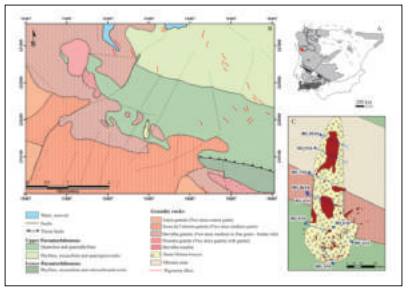

Figure 1 A. Iberian Variscan geotectonic zones (after Ribeiro et.al., 1990): GTMZ, Galicia Trás-os-Montes Zone; CIZ, Central Iberian Zone; OMZ, Ossa Morena Zone; SPZ, South Portuguese Zone: red star - Borralha area. B. Simplified geology of Borralha area based on 1/50 000 scale regional geological maps (6A - Montalegre (Noronha & Ribeiro, 1983), 6C - Cabeceiras de Basto (Ribeiro et al., 2001)), using coordinate system ETRS_1989_Portugal_TM06. C. Simplified geology of Santa Helena breccia with the projection of the drill holes made in the breccia body.

2.1.1. MINERALOGY

Petrographic studies, previously developed in samples collected from drill cores, made possible to observe some new mineralogical features from SHB. Four mineralization stages were defined: stage I - ilmenite ± cassiterite I ± apatite ± Th-U-REE phosphates ± muscovite I ± scheelite I ± Fe,Mn chlorite ± biotite ± quartz I; stage II - wolframite ± scheelite II ± Nb-W oxides ± muscovite II ± Fe chlorite ± quartz II; stage III - pyrite ± chalcopyrite ± sphalerite ± cassiterite II ± Mg, Fe chlorite; stage IV – molybdenite, bismutinite ± native bismuth ± galena ± minor sulphides (matildite ± aikinite± pavonite ± stannite ± greenockite) ± Fe,Mg chlorite ± quartz III (Gonçalves et al., 2016, Bobos & Noronha, 2017). There are three types of quartz in the breccia: a milky massif quartz (Qtz I), with no obvious mineralization, and a clearer one, with a greyish colour associated with wolframite (Qtz II) and a late hyaline quartz (Qtz III) associated with Fe,Mg chlorite (repidolite). Different forms of occurrence of the tungstates were defined: (i) disseminated fine (<1 mm) and very fine wolframite and scheelite association in the altered granite elements; (ii) disseminated medium (> 5 to 10 mm) to coarse (> 10 mm) wolframite associated with quartz II; and (iii) coarse (> 10 mm) wolframite crystals in late quartz veinlets cutting the breccia (Gonçalves et al., 2016).

3. MATERIALS AND METHODS

During 2014 and 2015, trenches, channels and 9 drills were carried out on SBH by Blackheath & Minerália consortium. A number of samples were collected from the drill cores and many polished thin-sections were made. Several analytical techniques were used in this study: optical microscopy, scanning electron microscopy with semi-quantitative elementary analyses (SEM-EDS) and geochemical analyses. Petrographic observations of polished thin-sections were performed at the Faculty of Sciences, University of Porto, using a stereomicroscope Zeiss Stemi SV11 Apo coupled with a Sony Cyber-Shot DSC-S75 digital camera and also using a Leica DM LSP polarizing microscope with transmitted and reflected light, coupled with a Leica camera with LAS EZ software 2.0.0. SEM-EDS analyses were performed at the Materials Centre of the University of Porto using an FEI Quanta 400 FEG-ESEM/EDAX Genesis X4M instrument. The SEM was operated at 15 kV in high-vacuum mode, manual aperture, and 4.5 beam spot sizes. The geochemical analyses were carried out by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by the accredited commercial laboratories of the ALS Group at Seville (Spain).

4.RESULTS AND DISCUSSION

4.1. LITHOLOGIC DESCRIPTION

The drilling campaign carried out on SHB was extremely important, because it provided important information about this body in depth. Different rock types were found constituting the breccia elements, which were always similar to the regional host rocks (Borralha tonalite, two-mica granite, Borralha granite, pegmatite, aplite and micaschists). These lithologies can occur as large metric blocks and it is difficult to recognize, in the drill core, if they are elements of the breccia. On the other hand, the breccia is well identified when the elements are centimetric. In this case, it is possible to distinguish the different regional lithologies (Fig. 2).

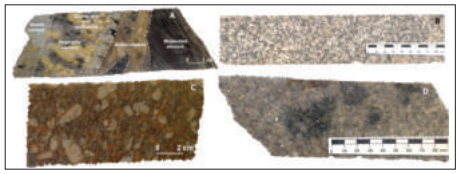

Figure 2 A. Representative sample of the SHB. It is possible to distinguish different elements: granite, pegmatite, aplite and mica-schist. The matrix is composed by quartz with wolframite. Also, it is possible to observe the presence of a late quartz vein cutting the elements. B. Sample of the regional two mica granite. C. Sample of the Borralha porphyritic biotite granite. D. Mineralized granite with fine wolframite.

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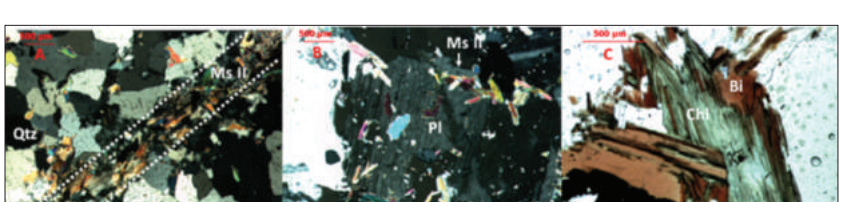

Figure 3 Some features of hydrothermal alteration present in Santa Helena breccia. A. Microphotograph in transmitted polarized light showing the occurrence of muscovite II (Ms II) with apparent oriented aspect. B. Microphotograph in transmitted light showing the replacement of plagioclase by muscovite II. C. Microphotograph in transmitted light showing the substitution of biotite (Bi) by chlorite (Chl).

4.2. HYDROTHERMAL ALTERATION

Hydrothermal alterations are visible in core samples (Fig. 2D) and at microscopic scale. These alterations appear with variable intensity and are characterized by muscovite I ± quartz II ± muscovite II ± chlorite (Fig. 3A). The hydrothermal alteration is more evident when the fragments are graniic, pegmatitic or aplitic. K-feldspar and plagioclase are partially replaced by quartz + muscovite II (Fig. 3B) and biotite ± chlorite (Fig. 3C). Muscovite I is represented by well-developed crystals (>500 µm) and muscovite II is characterized by small crystal (< 100 µm) agglomerates with a preferential oriented aspect. The hydrothermal alteration assemblage represented in the SHB is similar to the "greisen" with quartz, muscovite II and minor chlorite described by Alderton et al., (1980) for Cornwall granites. Usually, associated with this hydrothermal alteration occurs fine and dispersed wolframite and scheelite.

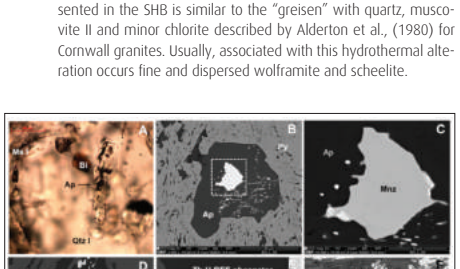

Figure 4 A. Microphotograph in transmitted light showing the association between apatite (Ap, (≈200 µm) and quartz (Qtz I), muscovite I (Ms I) and biotite (Bi). B, C. High-contrast, backscattered electron (BSE) microphotographs of apatite with large monazite inclusions (≈40 µm); a fine powdering of very small monazite inclusions (<5 µm) is visible in specific areas. D, E. BSE microphotographs showing the occurrence of fine Th-U-phosphate (≈10 µm) inclusions partially elongated and parallel to the apatite b axis. F. BSE microphotograph showing acicular monazite crystals intergrown with ilmenite (Ilm).

4.3. TH-U-REE PHOSPHATES

Petrographic observation also allowed identifying several accessory minerals, namely apatite, monazite and other REE phosphates. Apatite occurs as euhedral to sub-euhedral crystals (≈200 µm) with biotite, both included in quartz I (Fig. 4A) and in pyrite and also associated with ilmenite. Apatite includes fluid inclusions and minor mineral phases. Analyses performed in SEM-EDS allowed the identification of monazite and xenotime as inclusions in apatite. The monazite inclusions in apatite have different forms of occurrence; it is possible to observe the crystallization of moderate-sized monazite (≈40 µm) and/or very small inclusions (<5 µm) (Fig. 4B,C). Also, it is possible to observe the occurrence of fine Th-U-phosphate elongated inclusions parallel to the apatite b axis (Fig. 4D,E). In some cases, acicular monazite crystals occur intergrown with ilmenite (Fig. 4F).

4.3. GEOCHEMISTRY

To understand the role of the hydrothermal alteration in the occurrence and distribution of the REE in the breccia and in the regional granite rocks, we carried out the comparative study between hydrothermal altered lithologies and weakly/unaltered lithologies. We considered altered rocks represented by breccia samples and unaltered rocks represented by two-mica and biotite regional granites. Representative samples of the drill cores were selected and geochemical analyses were made. The two-mica granite is represented by samples 183 and 184, from the end of the core; the biotitic granite is represented by a sample from a large element, cut by the drill at 50 m, and by a sample from an outcrop.

REE data, required in geochemical analyses, are presented in Table 1. It is possible to observe that the samples corresponding to the breccia present the higher contents in REE (159.2 < $\Sigma REE_{breccia}$ < 309 ppm), with mean values in LREE of 209.09 ppm and mean values in HREE of 13.26 ppm. The granite rocks reveal different behaviours: the two-mica granite shows a ΣREE ranging from 40 to 58.6 ppm and Borralha biotite granite presents ΣREE ranging from 101.49 to 145.15 ppm. The mean contents in REE ($\bar{x}$ ≈ 222.34 ppm) of the breccia are always higher than in the regional granites.

In Fig. 5 are represented the REE spectra normalised to the chondrite contents (Evensen et al., 1978). The interpretation of the REE spectra allowed to the identification of two distinct behaviours in spite of similar profiles. It is possible to observe that the altered rocks, represented by breccia samples, always exhibit higher normalized values in REE, namely in LREE. We can also observe a similar behaviour if we compare a sample of Borralha granite from the core (50) with the composition of non-alterated granite (Bor1).

The circulation of magmatic-hydrothermal fluids promotes metasomatism where chemical compositions of a rock and/or mineral phases are modified in a pervasive way. Various studies have been performed to demonstrate that the major and trace elements are mobile during alteration processes (Humphris, 1984).

Therefore, there is increasing evidence that, during some alteration processes, the abundance of the REE, and their distribution patterns, when considered relative to chondrite elemental concentrations, may be changed sufficiently to affect significantly any petrogenic interpretation.

Geochemical analyses allowed the identification of higher contents of REE in the breccia (altered rock) than in the granitic facies (unaltered rock). This fact is controlled by the interaction between magmatic-hydrothermal fluids along boundaries and/or cracks in the rocks, which can modify and transport mobile elements, like major and trace elements (Harlov, 2015).

5. CONCLUSIONS

The study of hand samples and polish thin-sections allowed identifying different degrees of hydrothermal alteration. It was possible recognize that the hydrothermal alteration in the SHB is more intense than in the regional rocks. This alteration appears

TABLE 1. REE (PPM, CHONDRITE-NORMALIZED, EVENSEN ET AL., 1978) ANALYSES OF BRECCIA (18 – BRECCIA WITH TONALITE ELEMENTS, 28 – BRECCIA WITH SCHIST ELEMENTS, 56 – BRECCIA WITH QUARTZ VEINLETS, FINE SCHEELITE AND WOLFRAMITE, 67 – BRECCIA WITH WOLFRAMITE AND VESTIGIAL SCHEELITE, 89 – BRECCIA WITH FINE WOLFRAMITE, 96 – FRACTURED BRECCIA WITH VESTIGIAL WOLFRAMITE, 167 AND 169 – BRECCIA WITH FINE WOLFRAMITE AND SCHEELITE), TWO MICA GRANITE (183 AND 184 – TWO-MICA GRANITE WITH SOME SULPHIDES AND CHLORITE), CABREIRA GRANITE (91) AND BORRALHA PORPHYRITIC BIOTITE GRANITE (50 – ALTERED AND BOR1 – NO ALTERED). LREE: LIGHT RARE EARTH ELEMENTS; HREE: HEAVY RARE EARTH ELEMENTS

Samples	18	28	56	67	89	96	167	169	183	184	50	91	Bor1
La	71.4	83.8	31.3	38.9	38.8	38.8	47.3	54.9	62.2	9.9	7.9	12.0	21.22
Ce	130.5	143.5	64.1	77.1	74.8	80.8	98.5	109.5	124.0	21.1	17.3	27.3	45.35
Nd	55.7	56.6	25.3	31.0	30.1	33.7	39.3	43.0	45.8	9.0	7.4	11.3	21.65
Sm	9.1	9.0	4.4	4.9	4.5	5.8	6.5	7.4	7.6	2.8	2.2	2.7	4.97
Eu	1.4	1.3	0.7	0.8	0.8	0.9	0.8	0.8	1.1	0.3	0.2	0.3	0.6
Gd	7.1	6.2	3.4	3.7	3.7	4.7	5.3	5.3	5.4	2.7	2.2	2.3	3.88
Dy	5.2	4.4	2.7	3.2	3.1	4.3	4.1	3.7	3.8	1.9	1.8	1.4	2.22
Er	2.4	2.0	1.4	1.4	1.7	2.4	2.3	1.7	2.2	0.6	0.6	0.8	0.81
Yb	1.8	1.9	1.2	1.5	1.5	2.2	2.1	1.7	1.9	0.4	0.4	0.4	0.68
Lu	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.1	0.16	0.1	0.11
La*	291.9	342.6	128.0	159.0	158.6	158.6	193.4	224.4	254.3	40.5	32.3	49.1	86.8
Ce*	204.6	225.0	100.5	120.9	117.3	126.7	154.4	171.7	194.4	33.1	27.1	42.8	71.1
Nd*	117.6	119.5	53.4	65.4	63.5	71.1	82.9	90.8	96.7	19.0	15.6	23.8	45.7
Sm*	58.9	58.7	28.4	31.6	29.2	37.7	42.3	48.1	49.4	17.9	14.4	17.5	32.3
Eu*	23.3	22.4	12.2	14.0	14.3	15.2	14.3	14.5	19.6	5.0	4.0	5.2	10.3
Gd*	34.9	30.2	16.7	18.2	18.0	23.0	26.0	25.9	26.3	13.0	10.7	11.3	19.0
Dy*	20.3	17.3	10.7	12.6	12.1	16.9	16.1	14.7	15.0	7.6	7.0	5.5	8.7
Er*	14.4	12.1	8.3	8.6	10.1	14.2	13.9	10.4	13.1	3.8	3.6	4.8	4.9
Yb*	10.7	11.3	7.5	9.0	8.9	13.6	12.4	10.5	11.5	2.4	2.3	2.4	4.1
Lu*	9.8	11.4	6.3	8.3	10.6	11.8	12.2	10.2	11.8	2.0	1.6	3.9	4.33
LREE	268.0	294.2	152.7	149.0	160.0	192.4	215.7	240.7	43.0	35.0	125.8	53.6	93.8
HREE	16.7	14.7	10.1	10.2	13.9	14.1	12.8	13.6	5.7	5.0	8.9	5.0	7.7
∑REE	284.7	309.0	162.8	159.2	173.9	206.5	228.4	254.3	48.7	40.0	134.7	58.6	101.5
Eu/Eu*	0.5	0.5	0.6	0.6	0.5	0.4	0.4	0.5	0.3	0.3	0.5	0.4	0.4
Eu/Eu	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.14
La/Sm	7.9	9.3	8.0	8.6	6.7	7.3	7.4	8.2	3.6	3.6	7.1	4.4	4.27
La*/Sm*	5.0	5.8	5.0	5.4	4.2	4.6	4.7	5.2	2.3	2.3	4.5	2.8	2.69
Gd/Yb	4.0	3.3	2.5	2.5	2.1	2.6	3.0	2.8	6.6	5.7	2.8	5.8	5.71
Gd*/Yb*	3.3	2.7	2.0	2.0	1.7	2.1	2.5	2.3	5.4	4.6	2.2	4.6	4.61
La/Yb	40.3	44.8	26.1	26.4	17.3	23.1	31.6	32.7	24.8	20.8	25.4	30.0	3.21
La*/Yb*	27.2	30.2	17.6	17.8	11.7	15.6	21.3	22.1	16.7	14.0	17.2	20.2	21.06

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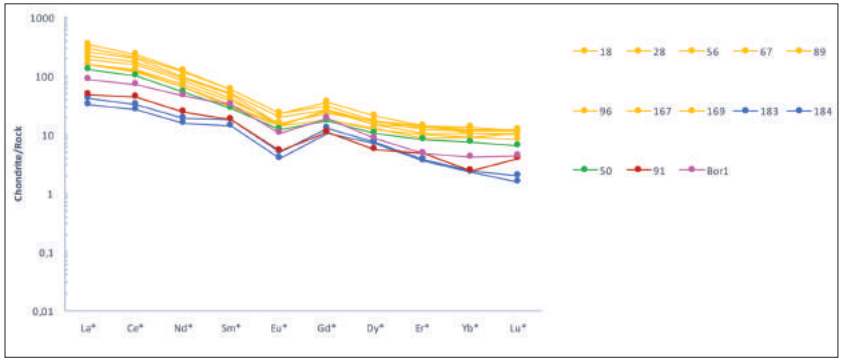

Figure 5 – REE spectra of the studied samples normalised to the chondrite contents (Evensen et al., 1978).

with variable intensity and is characterized firstly by muscovite I and, after, by quartz I ± muscovite II ± chlorite. Petrographic and SEM-EDS performed in samples from the breccia allowed the identification of apatite, monazite and other Th-U-REE phosphates as the principal hosts for REE. Apatite is the most common accessory mineral and the amount of REE can be metasomatically removed from apatite to form other REE-bearing minerals, such as monazite, which is commonly found as inclusions in apatite. Geochemical analyses performed in representative samples of breccia and regional granites showed an enrichment of REE in the breccia. This fact is controlled by the interaction between magmatic-hydrothermal fluid along boundaries and/or cracks in the rock, which can modify and transport mobile elements, like, major and trace elements. The results of this study showed that REE can be considered mobile during the fluid-rock interaction, in specifically in greisenization, related to magmatic-hydrothermal fluids, associated with a buried cupola of a late-orogenic granite, that implies a W, Ti, Sn, P, Th, U, REE mineralization.

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Statistical analysis of the geochemical data of the Santa Helena Breccia

Análise estatística dos dados de geoquímica da Brecha de Santa Helena

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Abstract: The Borralha deposit (Northern Portugal) was exploited for W and Cu, during the twentieth century, mainly from hydrothermal quartz veins containing wolframite, scheelite and sulphides. In addition to the veins, there also occur two mineralized breccia pipes: Santa Helena and Venise. This study intends to complement previous studies on the mineralogy of Santa Helena breccia, by using statistic studies applied to geochemical data. Two different statistic methods were used: determination of Pearson's correlation coefficients and cluster analysis. Our results show that the statistical analysis of the geochemical data corroborates the results previously published using other methodologies.

K**ey-words:** Borralha, Santa Helena Breccia, Pearson's correlation coefficients, cluster analysis.

Resumo: O depósito de Borralha (N de Portugal) foi explorado para W e Cu, durante o século XX, principalmente de filões de quartzo hidrotermais com volframite, scheelite e sulfuretos. Além dos filões, também ocorrem duas brechas mineralizadas: Santa Helena e Venise. Este trabalho tem como principal objetivo complementar os resultados obtidos através da utilização de outras metodologias relacionadas, essencialmente, com a mineralogia da brecha de Santa Helena, utilizando estudos estatísticos aplicados aos dados geoquímicos. Para alcançar este objetivo foram utilizados dois métodos estatísticos distintos: determinação dos coeficientes de correlação de Pearson e análise de *clusters*. Os nossos resultados mostram que a análise estatística dos dados geoquímicos corrobora os resultados mineralógicos previamente publicados.

Palavras-chave: Borralha, Brecha de Santa Helena, coeficientes de correlação de Pearson, análise de *clusters*.

INTRODUCTION

In the last century, Borralha was the second largest W mine in Portugal. The deeper underground works were down to level -210 (Level 0, corresponds to a height of 772 m), and have exploited vertical and sub-horizontal quartz veins. The main ore minerals were wolframite and scheelite. In addition to the vein structures, the Borralha deposit also has two mineralized breccia pipes with quartz cement, known as Santa Helena Breccia and Venise breccia. This contribution intends to complement results obtained in previous mineralogical studies from Santa Helena breccia, using statistical tools applied to geochemical data.

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GEOLOGICAL SETTING

Santa Helena Breccia (SHB) corresponds to an outcropping sub-vertical N-S structure cutting the NW-SE contact between the Borralha synorogenic granite and Paleozoic metasedimentary rocks. During 2014 and 2015, nine drill-holes were carried out on the SHB by Blackheath & Minerália consortium to recognize and evaluate the SHB potential for tungsten mineralization. Previous petrographic studies ran in these drill core samples have shown some new mineralogical characteristics and permitted to define four mineralization stages for mineral deposition (Gonçalves et al., 2016; Gonçalves & Noronha, 2017a,b; Bobos & Noronha, 2017)**:**

- *stage I* - ilmenite ± cassiterite I ± apatite ± Th-U-REE phosphates ± muscovite I ± scheelite I ± Fe, Mn chlorite ± biotite ± quartz I;
- *stage II* - wolframite ± scheelite II ± Nb-W oxides ± muscovite II ± Fe chlorite ± quartz II;
- *stage III* - pyrite ± chalcopyrite ± sphalerite ± cassiterite II ± Mg, Fe chlorite;
- *stage IV* – molybdenite, bismuthinite ± native bismuth ± galena ± minor sulphides (matildite ± aikinite± pavonite ± stannite ± greenockite) ± Fe, Mg chlorite ± quartz III.

MATERIALS AND METHODS

Geochemical analyses were carried out by the accredited commercial laboratories of the ALS Group Seville (Spain), by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The obtained geochemical results were processed by two different statistic methods: determination of Pearson's correlation coefficients and hierarchical cluster analysis based in Euclidean distance.

RESULTS

A. Correlation matrix based on the Pearson's correlation coefficients was stablished. The variables used to determine the correlation coefficients, in 100 samples, were: oxides of major elements (SiO_2, Al_2O_3, Fe_2O_3, K_2O, CaO, MnO, MgO, Na_2O, TiO_2, P_2O_5) and minor and trace elements (Sn, Cr, V, Cs, Ga, Nb, Sr, Y, U, Th, Ta, Hf, Ba, Rb, Zr, W, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Depending on the values of the correlation, several groups have been considered:

Strong positive correlation (r_{strong}>0.5, p<0.05):

- La with Ce (r=1.00), Pr (r=0.99), Nd (r=0.99) and Sm (r=0.93) suggesting an association with REE phosphates, such as, monazite and xenotime (*stage I*);
- P_2O_5 - CaO (r=0.9) consistent with the presence of apatite;
- TiO_2 - Fe_2O_3 (r=0.87), V (r=0.95) and Y (r=0.83) suggesting an association with ilmenite;

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- Zr - Hf (r=0.99) and Th (r=0.8) indicating a possible association with zircon;
- W - MnO (r=0.72) related to Mn-rich wolframite;
- W - Nb (r=0.66) confirming the presence of Nb and W oxides (*stage II*);
- Sn - Fe_2O_3 (r=0.6), Ga (r=0.8), Nb (r=0.6) and Ta (r=0.63) alluding the presence of cassiterite;
- Fe_2O_3 - MgO (r=0.84) and MnO (r=0.56) compatible with chlorite (*stage I* – Fe, Mn chlorite; *stage IV* – Fe, Mg chlorite).

It is possible to find other strong positive correlations between major elements denoting the relative abundance of other essential minerals phases, such as micas (Al_2O_3 and K_2O: r=0.82).

Intermediated positive correlation($0<r_{int}\leq 0.5$, $p<0.05$):

- CaO - Nb (r=0.5), Ta (r=0.47) and W (r=0.39), interpreted as indicating the occurrence of scheelite (stage I or II).

B. **Cluster analysis** was carried on using data from 110 samples and the following elements taken as variables: minor and trace elements (Sn, Cr, V, Cs, Ga, Nb, Sr, Y, U, Th, Ta, Hf, Ba, Rb, Zr, W, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) aiming the highlighting of groups of elements with similar geochemical behavior. In cluster analysis, the basic measurement of similarities and criteria for combining variables into clusters should be considered. In this study, the dendogram that best fitted our data was obtained using the Euclidean distance and Ward method. The results are illustrated in the dendogram of "Hierarchical Cluster Analyses" (Fig.1).

- A cluster analysis was initially carried out on the data set using 30 variables (Ba, Rb, Cr, V, Cs, Ga, Nb, Sr, Hf, Ta, Th, Y, U, Sn, Zr, W, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), once it has been considered very important to distinguish mineral phases enriched in minor and trace elements from tungstates. According to the results of cluster analysis (Fig.1A) two distinct groups can be identified. All the variables, except W, were clustered in one group (Cluster 1). This cluster represents mineral phases enriched in trace and minor elements, such as apatite, monazite, xenotime and other Th-U phosphates in the stage I. The second group (Cluster 2) represented by W, suggests the occurrence of wolframite and scheelite in stage II, and it does not have any relevant affinity with the measured minor and trace elements.
- The second cluster analysis was carried out on the data set using 15 variables (La, Nd, Ce, Tm, Lu, Eu, Tb, Ho, Yb, Er, Pr, Sm, Gd, Dy, P_2O_5). According the cluster analyses (Fig.1B), two distinct clusters can be identified. The variables La, Nd, Ce were clustered in one group (Cluster 1), can indicate the occurrence of zircon, presented in the granitic elements of the

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breccia, instead of REE phosphates (in stage I) because does not have an affinity with P_2O_5. The second cluster (Cluster 2) represented by P_2O_5, Tm, Lu, Eu, Tb, Ho, Yb, Er, Pr, Sm, Gd and Dy elements, reflects the occurrence of monazite and other phosphates that carry these elements in their structure.

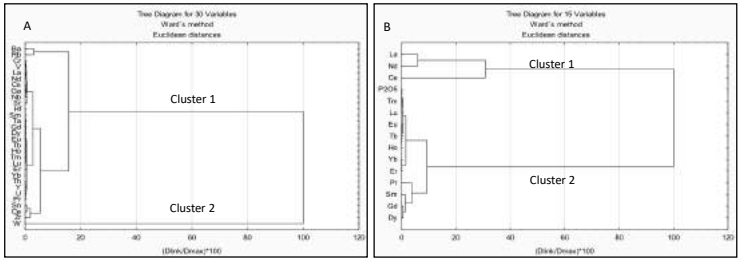

Figure 1. Dendogram showing hierarchical cluster analysis.

CONCLUSIONS

Pearson's correlation coefficients and cluster analysis provide reliable information on the mineral allocation of a significant number of elements, and on their crystallochemical affinities. Some trace elements and REE showed a strong affinity ($r_{strong}>0.5$, $p<0.05$), corresponding to the occurrence of apatite, monazite, xenotime and Th-U phosphates. Other strong positive correlations were identified, representing the association with wolframite, ilmenite, chlorite, cassiterite and zircon. It was possible to verify an intermediate positive correlation between CaO – Nb, Ta and W corresponding to the occurrence of scheelite. The results of cluster analyses suggested that this methodology might be used to identify groups of minerals based on the statistical behaviour of major, minor and REE elements. This study corroborates previous approaches based on the petrographic inspection and mineralogy of the SHB (e.g., Gonçalves & Noronha, 2017a,b; Bobos & Noronha, 2017).

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Geochemical characterization of Santa Helena Breccia (Borralha W Deposit, Northern Portugal)

Caraterização geoquímica da Brecha de Santa Helena (Jazigo de tungsténio da Borralha, Norte de Portugal)

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Abstract

One of the specificities of the Borralha W deposit is the occurrence of two breccia pipes. The most important and the only one that outcrop is the Santa Helena Breccia (SHB). It displays zones with a disseminated tungsten mineralization in zones with higher hydrothermal alteration. This hydrothermal alteration is characterized by the association of muscovite I and II ± quartz II ± chlorite, being more evident when the breccia fragments are of granite, pegmatite or aplite nature. In order to characterize SHB a geochemical study comparing the mineralized and the barren zones was undertaken. The geochemical composition shows an increase of MnO, Fe_2O_3, Al_2O_3, K_2O, Ba, Nb, Zr, Sn, W as well as REE in mineralized zones. The study of the major and trace elements geochemistry, in SHB, can help to discriminate zones with W mineralization.

Keywords: Santa Helena Breccia, tungsten mineralization, hydrothermal alteration, mineralized zones, geochemical characterization

Resumo

Uma das especificidades do jazigo de W da Borralha reside na ocorrência de duas chaminés brechóides (brechas). A brecha mais importante e a única aflorante é a de Santa Helena (BSH). Esta apresenta uma mineralização em tungsténio disseminada em zonas com intensa alteração hidrotermal. Esta alteração hidrotermal caracteriza-se pela associação entre moscovite I e II ± quartzo II ± clorite, sendo mais evidente quando os fragmentos da brecha são do tipo granito, pegmatito e pegmatito. Para caracterização da BSH foi realizado um estudo geoquímico comparativo entre zonas mineralizadas em tungsténio e zonas não mineralizados. A composição geoquímica mostra que existe aumento das concentrações de MnO, Fe_2O_3, Al_2O_3, K_2O, Ba, Nb, Zr, Sn W e REE em zonas mineralizadas. O estudo geoquímico da BSH, pode ajudar a discriminar zonas com mineralização em tungsténio.

Palavras-chave: Brecha de Santa Helena, mineralização de tungsténio, alteração hidrotermal, zonas mineralizadas, caraterização geoquímica

Introduction

In Portugal, the dominant W and Sn deposits are distributed all through the Central Iberian Zone - CIZ - and Galícia Trás-os-Montes Zone - GTMZ - forming the so-called "Iberian Sn-W Metallogenic Province" (Neiva, 1944). These deposits and many other similar ore-showings occur where Variscan granites intrude metasedimentary rocks (Precambrian to Silurian-Devonian). In the last century, Borralha was the second W mine in Portugal, after Panasqueira. The exploitation was elaborated in quartz veins enriched in wolframite and scheelite associated with other minor ore minerals. The Borralha deposit has the particularity to have, in addition to the veins, two breccia pipes: Santa Helena (SHB) and Venise. The SHB is the most important and the only one outcropping, being partially mined in the 50' because it is mineralized. The geochemical signatures of the SHB zones with evident W mineralization and those which are not mineralized, are compared to identify some possible geochemical parameters useful as an indirect method for tungsten exploration. To distinguish the zones with W mineralization the W grade proven by geochemical assays was considered. This study may provide a better understanding of the relationship between the grade of tungsten mineralization and the presence and type of hydrothermal alteration.

Geological setting

The Borralha area is located on the boundary between the CIZ and GTMZ (Fig. 1A). The dominant rocks outcropping in this area are Silurian metamorphic rocks and Variscan granitoids (Fig.1B). SHB corresponds to an outcropping sub-vertical N-S structure cutting the contact between the Borralha granitoids, metasedimentary rocks and a "mixture zone" (Fig. 1C). The fragments of the breccia are mainly angular, their sizes are very variable and it is essentially cemented by quartz. It is possible to find, side by side, metric blocks next to centimetric elements with a similar lithological composition to the surrounding regional rocks.

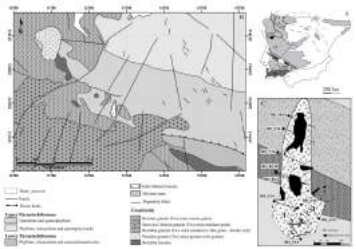

Fig. 1 - A. Iberian Variscan geotectonic zones, black star - Borralha area. B. Simplified geology of Borralha area based on 1/50000 scale geological maps. C. Simplified geology of SHB with the representation of the drill holes.

Mineralogy: Four mineralization stages were previously recognized (Gonçalves *et al.*, 2018 *in press*; Bobos & Noronha, 2017): stage I - ilm ± cst I ± ap ± Th-U-REE phosphates ± ms I ± sch I ± Fe, Mn chl ± bt ± qtz I; stage II - wf I and II ± sch II ± Nb-W oxides ± ms II ± Fe chl ± qtz II; stage III – main sulphides ± cst II ± Mg, Fe chl; stage IV – native bismuth ± minor sulphides ± Fe, Mg chl ± qtz III. The abbreviations used indicate the different mineral phases followed the symbols proposed by Cache (1956) and Kretz (1983). In the cores, it was possible to distinguish three modes of occurrence of the tungstates: (i) fine-grained (<1 mm) to very fine-grained wf and sch in the fragments; (ii) medium (> 5 to 10 mm) to coarse-grained (> 10 mm) wf in the cement; and (iii) coarse-grained (> 10 mm) wf in late qtz veinlets cutting the breccia.

Hydrothermal alteration is visible in core samples and at the microscopic scale. This alteration appears with variable intensity and is characterized by two generation of muscovite, quartz and four generations of chlorite. The hydrothermal alteration is more evident when the fragments are of granite, pegmatite or aplite where K-feldspar and plagioclase are partially replaced by qtz II + ms II and bt is replaced by chl (Gonçalves & Noronha, 2017). Associated with this hydrothermal alteration occurs fine-grained dispersed wolframite and

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scheelite. In a previous study, we investigate the REE behavior with hydrothermal alteration. It was possible to conclude that the mineralized samples present higher contents in REE (43 < ΣREE < 325.78) comparatively to barren samples (42.49 < ΣREE < 51.72) (Gonçalves & Noronha, 2017).

Materials and methods

During 2014 and 2015, trenches, channels and 9 drills were carried out on SBH by Blackheath & Minerália consortium. The geochemical analyses were carried out by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS) by ALS Group at Seville (Spain).

Results and discussion

Lithological description

Breccia fragments can correspond to big blocks and, in this case, it is difficult to recognize the breccia features. On the other hand, the breccia *s.r.* is well identified when the fragments are centimetric and angular with mineralized cement (Fig. 2B). It is also visible a random but consistent muscovite and/or sericite dissemination in the rocks or forming massive aggregates associated with the late quartz veinlets cutting the breccia. In this study, we select 7 representative samples of distinct lithologies present in zones with W mineralization and 1 sample of a barren granitic lithology (Table 1, Fig. 2).

Table 1 – Description of selected representative lithologies.

Associated with tungsten mineralization (W>200 ppm)	
Lithology	**Description**
Altered breccia	Fragments of pegmatite and micaschist; it is possible to observe hydrothermal alteration represented by small crystals of ms. W mineralization occurs in disseminated medium crystals of wolframite (wf) (Fig. 2A).
Breccia with quartz cement	Fragments of micaschist cemented by quartz; it is possible to observe hydrothermal alteration represented by small crystals of ms and some chl. W mineralization occurs in the qtz cement as medium to coarse-grained wf (Fig. 2B).
Altered pegmatite	Fragments of pegmatite in contact with micaschist. It is possible to observe the presence of random medium to coarse ms. W mineralization occurs as disseminated medium crystals of wf in the pegmatite fragment (Fig. 2C).
Altered fragment	Fragment of rock with granitic composition with strong hydrothermal alteration represented by fine to coarse ms and chl. In specific areas, fine-grained wf can be observed (Fig. 2D).
Leucocratic fragment	Fragment of rock with aplitic texture extremely altered. The alteration is represented by an intense muscovitization giving to the sample a light color (Fig. 2E).
Medium- to fine-grained two mica granite	Unaltered fragment of medium- to fine-grained two mica granite (Fig. 2F).
Late quartz vein with wolframite	Late quartz vein with clay minerals resulting from alteration of the K-feldspar and some oxides. It is possible to identify random chl. W mineralization is represented by coarse-grained wf (Fig. 2G).
Barren lithology (W<200 ppm)	
Granite	Fragment of medium- to coarse-grained two mica granite partially altered (Fig. 2H).

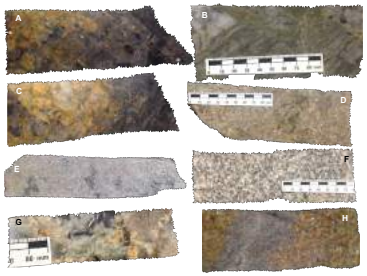

Fig. 2 – Representative samples of distinct lithologies presented in SHB. A – Altered breccia; B – Breccia with quartz cement; C – Altered pegmatite; D – Altered fragment; E – Leucocratic fragment; F – Medium- to fine- grained two-mica granite; G – Late quartz vein with wolframite; H – Cabreira granite. A-G: Lithologies presented in W mineralization zones. H: Barren lithology.

In fig. 3 the existence of two distinct groups is clearly evidenced: Group A representative of lithologies associated with W mineralization (W>200 ppm) including altered breccia, breccia with quartz cement, altered pegmatite, altered fragment, leucocratic fragment, medium- to fine- grained two-mica granite and late quartz with wolframite; and Group B embracing samples from barren granite (W<200 ppm).

Major element geochemistry

The major element composition of the studied lithologies shows a clear increase of some elements in mineralized lithologies compared with the barren ones (Table 2): (i) FeO_{total}, MnO and MgO suggesting the presence of disseminated wolframite ($(Fe,Mn)WO_4$) and chlorite; (ii) K_2O and Al_2O_3 associated with the hydrothermal alteration characterized by a potassic alteration.

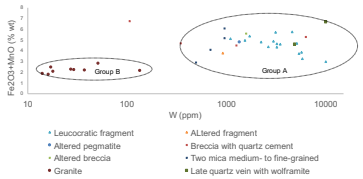

Fig. 3 – Fe_2O_3+MnO (% wt) – W (ppm) binary diagram showing composition of lithologies associated with W mineralization (Group A) and the Cabreira granite (Group B).

Table 2 - Minimum (min) and maximum (max) major element composition (% wt) of lithologies associated with tungsten mineralization (mineralized) and non-associated with tungsten mineralization (barren).

Element (% wt)	Mineralized (min-max)	Barren (min-max)
SiO_2	67.1-75.7	71.7-76.1
Al_2O_3	12.3-17.4	13.9-14.45
Fe_2O_{total}	2.38-4.86	1.61-2.38
CaO	0.21-1.25	0.49-0.71
MgO	0.40-1.33	0.25-0.42
Na_2O	0.18-2.69	1.07-2.85
K_2O	3.71-4.98	3.43-4.73
TiO_2	0.16-0.71	0.12-0.2
MnO	0.05-0.19	0.03-0.04
P_2O_5	0.12-0.61	0.35-0.44

Trace element geochemistry

The trace element composition of the two groups of lithologies show a large variation because they were collected from a heterogeneous body and represent different types of rocks. Therefore, the trace element composition for these lithologies is reported in the form of mean values in fig. 4. In the trace element variation diagram, it is possible to identify two distinct behaviors (B1 and B2). The B1 is representative of the lithologies present in mineralized zones and it is possible to observe an enrichment in Ba, Nb, Zr, Sn and W compared to barren lithologies (B2). On the other hand, the elements Rb and Sr do not show a distinct variation. The most significant variation is observed in W, as expected.

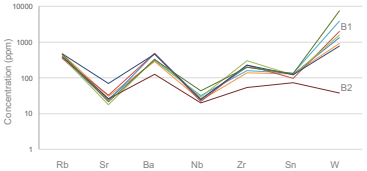

Fig. 4 – Trace element variation diagram for the lithologies presented in distinct zones of SHB. Colours used are the same that in fig 3.

Conclusions

To discriminate the ore potentially of distinct zones, the geochemical results must be combined with the geological data. The geochemical composition of the mineralized zones shows an increase of MnO, Fe_2O_3, MgO, Al_2O_3, K_2O, Ba, Nb, Zr, Sn, W as well as REE. The study of the major and trace elements geochemistry, in SHB, can help to discriminate zones with W mineralization.

Acknowledgements

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