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

PICO – EGU2018-16190

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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**

- **Santa Helena Breccia (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.

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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**;

![Diagram showing the Santa Helena Breccia Sector](image)

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

PICO viewing – EGU2018-16190 – other studies

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Santa Helena Breccia
Other studies

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Occurrence of the W mineralogy in the drill cores
Geochemical characterization of the Santa Helena breccia
Mineralization stages
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Stage II (W ± Nb-Ta)
Stage III (Fe-Cu-Zn ± Mo ± Sn)
Stage IV (Bi ± Pb ± Te-Ag)

Hydrothermal alteration in hand samples
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Distribution and mobility of REE during the hydrothermal alteration

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Background

- **Borralha mine** (1904-1985) was the 2\textsuperscript{nd} 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 2\textsuperscript{nd} 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\textsubscript{3}), was estimated at about 18,500 t.
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.
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 symbology used in fig. 3. B. 3D model of SHB located in Borralha W Mine (model provided by the Consortium Blackheath and Mineralia Lda.)
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.).
Distribution of the W contents in depth

- **Geochemical values** collected in **different lithologies** allowed to analyse 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 oxidized 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.
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.

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**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.
Geochemical characterization of the Santa Helena breccia

### Associated with tungsten mineralization (W>200 ppm)

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Altered breccia</td>
<td>Pegmatite and micaschist; hydrothermal alteration represented by small crystals of muscovite (ms); disseminated medium crystals of wolframite (wf) (Fig. A).</td>
</tr>
<tr>
<td>Breccia with quartz cement</td>
<td>Micaschist cemented by quartz; hydrothermal alteration represented by small crystals of ms and some chl; medium to coarse-grained wf (Fig. B).</td>
</tr>
<tr>
<td>Altered pegmatite</td>
<td>Pegmatite and micaschist; presence of random medium to coarse-grained ms; disseminated medium crystals of wf in the pegmatite fragment (Fig. C).</td>
</tr>
<tr>
<td>Altered fragment</td>
<td>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).</td>
</tr>
<tr>
<td>Leucocratic fragment</td>
<td>Lithology with aplite texture extremely altered. The alteration is represented by an intense muscovitization giving to the sample a light color (Fig. E). Disseminated wf.</td>
</tr>
<tr>
<td>Fine- to medium-grained two mica granite</td>
<td>Apparently unaltered fragment of medium- to fine-grained two mica granite (Fig. 2). Disseminated wf.</td>
</tr>
<tr>
<td>Late quartz vein with wolframite</td>
<td>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).</td>
</tr>
</tbody>
</table>

### Barren lithology (W<200 ppm)

<table>
<thead>
<tr>
<th>Lithology</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium- to coarse-grained two mica granite</td>
<td>Medium- to coarse-grained two mica granite partially altered (Fig. H).</td>
</tr>
</tbody>
</table>

Fig. 8 Representative samples from each lithology that composes de SHB. See Gonçalves et al., 2018 - CNG
Geochemical characterization of the Santa Helena breccia

Fig. 9 $\text{Fe}_2\text{O}_3+\text{MnO}$ (% 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).
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:
  - $\text{FeO}_{\text{total}}$, $\text{MnO}$ and $\text{MgO}$ suggesting the presence of disseminated ** wolframite** ((Fe,Mn)WO$_4$) and **chlorite**;
  - Higher values of $\text{CaO}$ can suggest the existence of **scheelite**;
  - $\text{K}_2\text{O}$ and $\text{Al}_2\text{O}_3$ associated with the hydrothermal alteration characterized by a **potassic hydrothermal alteration**.

<table>
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<tr>
<th>Element (% wt)</th>
<th>Mineralized (min-max)</th>
<th>Barren (min-max)</th>
</tr>
</thead>
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<td>$\text{SiO}_2$</td>
<td>67.1-75.7</td>
<td>71.7-76.1</td>
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<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>12.3-17.4</td>
<td>13.9-14.45</td>
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<tr>
<td>$\text{FeO}_{\text{total}}$</td>
<td>2.38-4.86</td>
<td>1.61-2.38</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>0.21-1.25</td>
<td>0.49-0.71</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>0.40-1.33</td>
<td>0.25-0.42</td>
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<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0.18-2.69</td>
<td>1.07-2.85</td>
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<tr>
<td>$\text{K}_2\text{O}$</td>
<td>3.71-4.98</td>
<td>3.43-4.73</td>
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<tr>
<td>$\text{TiO}_2$</td>
<td>0.16-0.71</td>
<td>0.12-0.2</td>
</tr>
<tr>
<td>$\text{MnO}$</td>
<td>0.05-0.19</td>
<td>0.03-0.04</td>
</tr>
<tr>
<td>$\text{P}_2\text{O}_5$</td>
<td>0.12-0.61</td>
<td>0.35-0.44</td>
</tr>
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</table>
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

![Graph showing trace element variation](image)

*Fig. 10 Trace element variation diagram for the lithologies presented in distinct zones of SHB. Colours used are the same that in fig. 9.*
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).
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.
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.
(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: Nb₂O₅ (56.846%), WO₃ (13.72%), MnO (12.045%), FeO (8.153%), TiO₂ (3.753%) and Ta₂O₅ (3.527%).

See Gonçalves and Noronha, 2017 - Goldschmidt2017
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).
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).
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.*
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.
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.
Breccia (n=8) – altered samples
- $159.2 < \Sigma$REE $< 309$ ppm
- LREE$_{mean}$ of $209.09$ ppm and HREE$_{mean}$ of $13.26$ ppm

Porphyritic biotite granite (Borralha granite, $n=2$)
- $50 – altered$ sample: $\Sigma$REE $= 134.7$ ppm
- Bor1 – unaltered sample: $\Sigma$REE $= 101.5$ ppm

Two-mica fine-grained peraluminous granites ($n=2$) – unaltered samples
- $40.0 < \Sigma$REE $< 48.7$ ppm

Two-mica medium grained peraluminous granite ($n=1$) – unaltered sample
- $\Sigma$REE$=58.6$ ppm

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

<table>
<thead>
<tr>
<th>Samples</th>
<th>18</th>
<th>28</th>
<th>56</th>
<th>67</th>
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<th>95</th>
<th>167</th>
<th>169</th>
<th>183</th>
<th>184</th>
<th>50</th>
<th>91</th>
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<td>La</td>
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<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.16</td>
<td>0.1</td>
<td>0.11</td>
</tr>
</tbody>
</table>

LREE: La-Gd and HREE: Dy-Lu – normalised to the chondrite contents (Evensen et al., 1978)
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.
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, Fe₂O₃, MgO, Al₂O₃, K₂O, 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 Pearson’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;
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.
References


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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 Vénice 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 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) and with minor expression, estanite, matildite, greenockite, bismuto nativo, galena and 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/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 (paraautochthonous terranes) in Borralha area (Montalegre). It corresponds to a sub-vertical structure cutting the contact between syenotic 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 veinslets with coarse wolframite cutting the breccia.

**FIGURE 1. DISTRIBUTION OF W-Sn DEPOSITS IN NORTHERN PORTUGAL.**

**FIGURE 2. LOCATION AND GEOLOGICAL SETTING OF THE SANTA HELENA BRECCIA IN THE BORRALHA AREA [5].**
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.

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 occurapatite, 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). 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, greencokite, 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 with vermicular chlorite.
Rare-metal mineralization associated with a Variscan breccia pipe

Borralha, N Portugal

A. Gonçalves, F. Noronha

I. Introduction

A large number of W deposits and occurrences are present in the Northwest of the Iberian Variscan Belt. In Portugal, the prevailing W and Sn deposits are distributed through the Central Iberian Zone (CIZ) and Galicia-Trás-Os-Montes Zone (GTZM), forming the “Iberian W-Sn Metallogenic Province” [1] included in the “Northern Iberian Metallogenic Province” [2] characterized by the presence of various 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 GTZM (Figure 1A). The dominant rocks types outcropping in this area are Silurian metamorphic rocks and Variscan granites (Figure 1B).

1.1. Santa Helena breccia (SHB)

The Santa Helena breccia pipe corresponds to an outpouring sub-vertical N-S structure cutting the NW-SE contact between the porphyritic biotite granite (Pyro I) and Borralha granite, metasedimentary rocks and a zone characterized by an association of Borralha granite with big panels of metasedimentary rocks, the “Moiture zone” [3] (Figure 1C). The contacts of the breccia are marked by N-S faults filled with massive barren quartz. Detailed geology, surface geological mapping and recent drilling indicate that it may be at least 575 m in length, over 150 m in width and 250 m in depth (known N-S-110°). The elements of the breccia are mainly angular and their sizes are very ranging (from centimetres to metres) with similar lithological composition to the surrounding regional rocks (e.g. granites, tonalites, pegmatites, aplites and mica schists) (Figure 1D). This breccia is interpreted as a collapse breccia (Noronha,1979).

II.1.1. Occurrence of the ore minerals

- Disseminated fine (â¼1 mm) and very fine wolframite and scheelite associated with altered granitic elements
- Disseminated medium (5 â¼ 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: Disseminated wolframite I (â¼1 mm) and also contain ore elements, the sulphidic stage associated with the sulphidic stage of the Sa Province.
- Stage II: wolframite II (4-6 µm) and scheelite II ± Nb-W oxides ± molybdenite ± galena ± zircon ± zircon ± zircon (granitoid) ± Fe, Mn, chlore I II and quartz III.

II. Materials and Methods

During 2013 and 2014, trenches, channels and drill holes were carried out on SHB by “Blackhead & Minerals” consortium. New representative samples were collected and several analytical techniques were used:

- Optical Microscopy
- Scanning Electron Microscopy with Semi-quantitative Elemental Analyses (SEM-EDS)
- 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):

- W I occurs in euhedral crystals (â¼50 µm) associated with a Fe, Mn mineral (Figure 2A) and the Sch II (â¼50 µm) occur replacing the first generation of wolframite (Figure 2B).
- W I occurs as well-developed subhedral crystals (â¼500 µm) and the wolframite II, only observed in SEM-EDS, as small subhedral crystals (â¼10 µm) in late fractures cutting wolframite II (Figure 2C).
- Associated with wolframite I we can find small crystals (5 - 20 µm) of a niobium-tungstate, columbo-tantulate, monazite and fluorspar (Figure 2D).  
- Electron Microprobe analyses were performed in wolframite, scheelite and niobium-tungstate (Table 1).

- The W I presents a MoO and MoO2 average content 5.74%, and W II is characterized by an enrichment in MoO2 (14.49%) consequently a composition of a tungsten-hydromolybdenum.
- Two generations of scheelite exhibit similar composition, however, Sch I presents some MoO2 (0.05%) and Sch II some FeO (0.11%). In any generation of scheelite is possible to find MoO2.
- The niobium-tungstate exhibits a complex geochemical composition where the most important oxides are: Nb2O5 (56.84%), WO3 (13.72%), MoO3 (12.04%), FeO (8.15%), TiO2 (1.93%) and Ta2O5 (0.52%).
- The oxides exhibit a complex internal texture characterized by a zoning at the microscale, resulting from the different phases of crystallization and the ratio Nb/Ta 1.37% can allowed a magmatic source for these mineral phases [5].

V. Conclusions

The described mineral assemblages and their dispersed mode of occurrence in a breccia with a large volume (20.5 M) correspond to a new tungsten mineralization type in the Iberian Peninsula. This 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.

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

Breacha de Santa Helena (Borralha – N Portugal). Um novo tipo de jazigo de tungsténio na Província Metalógénica 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, there 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-Re), 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: Brechá, 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 mineralizados: brecha de Santa Helena (BSH) e brecha Venise. O presente trabalho tem como objetivo principal contribuir para o estudo da BSH, e por isso, foram analisadas alterações hidotérmicas com intensidade variável no contato entre fragmentos da brecha com o cimento e em fraturas tardias. Estas alterações são caracterizadas pela ocorrência de duas gerações de muscovita, quartas e quatro gerações de clorito. Este estudo permitiu identificar quatro estádios de mineralização: Época I (Ti-Sn-W-Re), Época II (W-REE), Época III (Fe-Cu-Zn-Mo-Sb) e Época IV (Bi-Pb-Ag). A ocorrência de mineralização disseminada em brechas de grandes volumes corresponde a um novo tipo de depósito de tungstênio na Província Metalógénica de Estano-Tungstífera Ibérica.

Palavras-chave: Brechá, pipe breccia, tungstates, alteration, mineralization stages.

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1. Introduction

Hydrothermal ore deposits are big geochemical anomalies in the Earth that provide us the clearest evidence of the past flow of solutions through fault structures and porous rocks that, in the process, dissolve, transport and concentrated elements of economic interest (Wilkinson, 2001). In Portugal, the prevailing W and Sn in bed deposits are distributed all through the Central Iberian Zone - CIZ and Galiza Trás-os-Montes Zone - GTMZ (Jaliguert et al., 1975; Ribeiro, 2006), forming the so-called “Iberian-SW Metallogenic Province” (Neiva, 1944), included in the “Iberian “Northern Mineralogical Province” of the North Portuguese Province” (Neiva, 1944; Neiva, 1965) characterized by the presence of various W, W-Sn, W-Mo and Sn 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 granite–grano intrusion, followed by the formation of diapirs and breccia pipes: Santa Helena breccia (BSH) and Venise breccia.

2. Geological setting

Borralha area (Montalegre) is located at the Northwest of the Iberian Peninsula in the boundary between the CIZ (autochthonous terranes, Ribeiro, 1990, Ribeiro, 2006) and GTMZ (paraautochthonous 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 distinguished: syn-D3 granitoids (Borralha tonalite and Borralha granite, syn-D3 granites (Sierra de Cabreia 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 NS structure cutting the contact between syn-D3 granitoids (Borralha), metasedimentary rocks (Silurian in age) and a “Mixture zone” characterized by inclining 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 NS quartz veins. Detailed historical underground, surface geological mapping and recent drilling of SHB indicate it is about 757 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 presence 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, granite or any kind 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, Zn, Mo and Nb-Sn. It is an important source of metals and/or source of heat needed to cut the breccia, is recognizable and it must be remembered that the first exploitations of SHB in upper levels occurred in pen pits exploited in open pits.

Figure 1: Iberian Variscan tectonostratigraphic units (after Ribeiro & Sanderson, 1996 in Onizume et al., 2003); GTMZ, Galiza Trás-os-Montes Zone; CIZ, Central Iberian Zone; OME, Ossa Morena Zone; SPT, South Portugal Zone; a - images of the breccia pipes (SHB and BSH) 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; Hariaux et al., 2015a, b).
3. Materials and Methods

For this study, two drill cores were selected, BO_5/14 and BO_6a/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 element 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-S57 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 occurrence of 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 cement: a milky mass quartz (quartz I), with no obvious mineralization, a clearer one (quartz II) with a greyish tint associated with mineralization and a late hyaline quartz (quartz III). It is also visible a random but consistent muscovite I and II (muscovite II mineralization and a late hyaline quartz (quartz III). It is also possible to identify in the quartz II, occurring in subhedral to anhedral grains and medium-grained wolframite (Table 1).

![Figure 2](image2.png)  
**Figure 2.** Representative sample of Santa Helena breccia where is possible to observe angular fragments with distinct composition.

![Figure 3](image3.png)  
**Figure 3.** A. Pictorial log from BO_8a/14 drill core in Santa Helena breccia: a – grained tonalitic granite; b – breccia more tonalitic; c – grained wolframite granite with quartz vein level; d – quartz vein from W feldspar; e – very fractured breccia more schist with some oxidation; f – grained level of the breccia; g – fractured breccia with oxidation; h – breccia fractured with some oxidation and boxworks with medium-grained wolframite; i – grained breccia with some sulphides, some oxidation and sometime gauged. B. Distribution in depth of the quartz contents and their relationship with different types of thin-sections; a – i are previously mentioned description.

![Figure 4](image4.png)  
**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.

![Figure 5](image5.png)  
**Figure 5.** Distribution of the oxide, hydroxide, carbonate and sulphide phases, including Bi-rich secondary phases in 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.

![Figure 6](image6.png)  
**Figure 6.** Mode of occurrence of the Cu 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.

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 stutages 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).

4.3. Petrography

The petrographic study of the selected samples made possible to observe some mineralogical features of SHB. It must be emphasized that the occurrence of the wolframite 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 ± Mn ± Sn) and Stage IV (Bi ± Pb ± Ag).

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

The crystals of quartz occur in subhedral grains and vary in dimension from 500 (-500 μm), 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) clusged 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 later crystallization of these silicates. Small crystals of cassiterite (cst, <50 μm) also occur associated with muscovite I. Bi-rich (200 to 400 μm) sometimes replaced by chlorite, quartz (>200 μm) with inclusions of monazite, zircon and U. The REE phosphates (<200 μm) also occurs in this stage (Fig. 5B). A first generation of scheelite (Sch I) is also present in the thin-section occurring in sub-euhedral well-developed crystals (>500 μm) associated with Fe, Mn chloride 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 chloride, suggesting a crystallization in the void spaces (<500 μm) and including cassiterite (Fig. 5D); (ii) very fine-grained crystals (<200 μm) replacing ilmenite (Fig. 5E), and (iii) 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 contemporaneous relationship between the main sulphides of pyrite (Py, 200 to 400 μm), chalcopyrite (Cu ± Zn ± Sn, 500 μm), sphalerite (Sp >500 μm) (Fig. 5J), Mg, Fe chloride and adularia. The main sulphides occur associated with pre-existing muscovite I and II ± quartz and, it is possible to observe traces of small crystals of nodularbenedite (<100 μm). A second generation of cassiterite (50 to 100 μm) occurs filling late fractures (Fig. 5K).

4.3.4. Stage IV (Bi ± Pb ± Ag)

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

5. Discussion and Conclusions

Borralha has the particularity to have, in addition of the quartz veins, 1970 and 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 noted in each stage of a stage I were scheelite occur associated with molybdenite, cassiterite andREE phosphates and a second stage with wolframite, scheelite and Nb-Ta oxides. The already recorded volume of the breccia, 22.5 M tons, above 60 level, and the indiscriminate 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”.

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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 mineralisation, adding to this deposits occur two breccia bodies: Santa Helena Breccia (SHB) and Vence 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 ± muscovite ± quartz ± ilmenite; stage II- wolframite I ± Nb-W oxides ± muscovite ± W ± Zr ± Ce ± Hf; stage III- pyrite ± chalcopyrite ± scheelite ± cassiterite II; stage IV- wolframite II ± scheelite II ± (stannite, molybdenite, maldonite, greenschist, native bismuth, galena and sulphosalts (Te, Ag)) ± Zr ± Ce ± Hf. There are several hydrothermal alterations of the contact between the Santa Helena Breccia (Borralha) and the Meseta granitoids, mainly by fluids of continental origin (Borralha, CIF). This deposit was exploited during the last century, mainly with the use of open-cut mining. The Santa Helena deposit is an important example of disseminated tungsten mineralization in Variscan orogenies, with a potential for future exploration.

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 responsible for the mobilisation and deposition of metallic elements, so that the hydrothermal tungsten mineralisations 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 (zouliccothorium terranes) and the western part of Sào-Tiago-de-Montes zone (paratauxiccothorium terranes).

Santa Helena Breccia (SHB)

It is a body corresponding to a sub-vertical structure, with a 4.5 m 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-SW contact between a syntectonic biotite granite (Borralha granite) and metasedimentary rocks (Iberian 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 mineralisation is characterised by the association of W, Cu, Zn, Mo and minor Nb, Sn, Th, U, REE, Bi, Ag, Pb. SHB corresponds to an extraordinary example of a tungsten deposit in the Iberian orogeny.

Methods and Materials

The studied samples were obtained from a 10 drill cores campaign during 2014 made by the consortium Blackburn - Mineraç. From those were selected the drill core Bo_S_3/14 and Bo_Ba/14 (Figure 2). These samples were described macroscopically and after were studied with the recourse of several analytical techniques such as:

- Optical microscopy;
- Scanning electron microscopy (SEM-EDS);
- Geochemistry.

Mineralization in the drilling cores

Macroscopically, we identified five wolframite and scheelite associated with quartz and muscovite in the “matrix” elements and medium to coarse wolframite associated with quartz (Figure 3A). There were also identified several quartz veins associated with coarse wolframite crystals (Figure 3B).

Mineralogy

Stage I- Ilmenite ± cassiterite I ± Th-U and REE phosphates ± scheelite ± muscovite ± quartz ± ilmenite.

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

Stage II- wolframite I ± Nb-W oxides ± muscovite ± Zr ± Ce ± Hf.

This stage 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 zircons II (Figure 4D).

Stage III- main sulphides (pyrite, chalcopyrite, sphalerite) and cassiterite II ± Zr ± Ce ± Hf.

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

Stage IV- wolframite II ± scheelite II ± cassiterite II ± stannite, molybdenite, bismuthinite, maldonite, 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 mainly 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. Jay quartz ± muscovite II and different chlorine types.

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

Conclusions

In this study were identified four stages of mineralization: stage I- Ilmenite ± cassiterite I ± Th-U and REE phosphates ± scheelite ± muscovite ± quartz ± ilmenite; stage II- wolframite I ± Nb-W oxides ± muscovite ± Fe,Mn-chlorite; stage III- pyrite ± chalcopyrite ± scheelite ± cassiterite II; stage IV- wolframite II ± scheelite II ± (stannite, molybdenite, maldonite, greenschist, 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 the Iberian Variscan Tungsten Province.

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ABSTRACT
The Borrálha 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 comprising 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 granitization) 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, Borrálha W deposit

1. INTRODUCTION
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 (GTZ) (Ribiero et al., 1990) forming the so-called “Iberian Sn-W Metallogenic Province” (Neiva, 1944), included in the “Northern Metallogenic Province” (Thudeu, 1965) characterized by the presence of various W, Sn(5), 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. Thudeu, 1977). In the last century, Borrálha was the second W mine in Portugal. The deeper underground works were at level -210 (Level 0), the river Borrálha level, is at a height of 722 m exploiting vertical quartz veins (more than 45° dip) and sub-horizontal quartz veins (less than 30° dip). Major ore minerals are wolframite and scheelite associated with minor ore minerals like chlorapatite, 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 1941 until the closing of Borrálha, was estimated at about 18500 t (Noronha, 1983). Borrálha deposit has the particularity to have, in 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 50's of the last century, because it has tungsten mineralization in its cement and in ore shoots (“ore pockets”), and it was named as “stock-work”. In the European Variscan belt only one more example of breccia pipe was studied, Pay les Vignes in the French Massif Central (Cuney et al., 2002, Harlaut et al., 2015a,b).

2. GEOLOGICAL SETTING
Borrálha area (Montelégre) is located at the northwest of the Iberian Peninsulas in the boundary between the CIZ (autunhotonous terrain) and GTZ (parautochthonous and allochthonous terranes) (Fig. 1A). The dominant rocks types outcropping in this area are Silurian metatorphic rocks and Variscan granites. It is possible to distinguish different types of synorogenic granites: syn-D3 porphyritic biotite granite (Borrálha granite) and two-mica paraluminous granites, the most abundant regional granites, and a post-D3 leucocratic granite (Penedos granite) considered as related to Gebs late-orogenic massif (Nortonh & Ribiero, 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 Borrálha granite, metasedimentary rocks and a zone characterized by Borrálha granite with big panels of metasedimentary rocks, known as the “Mixture zone” (Nortonh, 1979) (Fig. 1C). The contacts of the brecca are marked by faults with massive barren quartz. Detalled 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 Ribiero et al., 1990). GTZ, Galicia Trás-os-Montes Zone, CIZ, Central Iberian Zone; GMZ, Ossa Morena Zone; SPZ, South Portuguese Zone; red star – Borrálha area. B. Simplified geology of Borrálha area based on 1:5 000 scale regional geological maps (A – Montalegre (Noronha & Ribiero, 1983), C – Cabeceras de Busto (Ribiero et al., 2001)), using coordinate system ETRS_1989_Portugal_1M0G.E. C. Simplified geology of Santa Helena breccia with the projection of the drill holes made in the breccia body (modified after Noronha et al., 1994).

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 ± ilmenite ± Th-U-REE phosphates ± muscovite ± scheelite ± Fe/Mn-chlorite ± biotite ± quartz ± ilmenite; stage II - wolframite ± scheelite ± Nb-Oxides ± muscovite ± Fe-Chlorite ± quartz; stage III - pyrite ± chlorapatite ± sphalerite ± cassiterite ± Fe-Mg-Chlorite; stage IV - molybdenite, bismuthite ± native bismuth ± galena ± minor sulphides (maltite + native bismuth + cancrinite + stannite + greenerite) ± Fe-Mg-Chlorite ± quartz (Ribiero et al., 2016; Bião & Noronha, 2017). There are three types of quartz in the breccia: a milky 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 (epidote). 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) 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, 15 core samples, channels and 9 drill were carried out on SHB by Blackshear & Minerals consortium. A number of samples were collected from the drill cores and many polished thin-sections were made. Several analytical techniques were used in thin-section, 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 Apollo 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-ESM/EDAX Genesis XAM 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).

3.1. 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 (Borrálha tonalite, two-mica granite, Borrálha granite, pegmatite, aplite and micaschist). 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).

4. RESULTS AND DISCUSSION
4.1. 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 ± ilmenite ± Th-U-REE phosphates ± muscovite ± scheelite ± Fe/Mn-chlorite ± biotite ± quartz ± ilmenite; stage II - wolframite ± scheelite ± Nb-Oxides ± muscovite ± Fe-Chlorite ± quartz; stage III - pyrite ± chlorapatite ± sphalerite ± cassiterite ± Fe-Mg-Chlorite; stage IV - molybdenite, bismuthite ± native bismuth ± galena ± minor sulphides (maltite + native bismuth + cancrinite + stannite + greenerite) ± Fe-Mg-Chlorite ± quartz (Ribiero et al., 2016; Bião & Noronha, 2017). There are three types of quartz in the breccia: a milky 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 (epidote). 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) 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).

Figure 2. 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 Borrálha porphyritic biotite granite. D. Mineralized granite with fine wolframite.
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 ± quartz II ± muscovite II ± chlorite (Fig. 3A). The hydrothermal alteration is more evident when the fragments are granitic, pegmatitic or aplatic. 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) aggregates with a preferential oriented aspect. The hydrothermal alteration assemblage represented in the SHI is similar to the “geisien” with quartz, muscovite II and minor chlorite described by Alderton et al. (1996), for Cornwall granites. Usually, associated with this hydrothermal alteration occurs fine and dispersed wolframite and scheelite.

4.3. TH-U-REE PHOSPHATES

Petrographic observation also identified 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 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 (~65 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,F). 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 weathed/unaltered lithologies. We considered different breccia types: REE-rich breccia, REE-depleted breccia and unaltered rocks represented by two-mica and biotite regional grano- styles. 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 biotite 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 (+0.9 µmol SrREE/Eu²⁰⁺ < 3.09 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 SrREE ranging from 40 to 59.6 ppm and Cornwall biotite granite presents SrREE ranging from 101.49 to 145.15 ppm. The mean contents in REE (+...2.32 ppm) of the breccia are always higher than in the regional granites.

In Fig. 5, the REE spectra are briefly described. The REE spectra is 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 LREE, namely in LREE. We can also observe a similar behaviour if we compare a sample of Cornwallite (0.5) with the composition of the non-altered granite (Borl’i). 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, 1989).

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 (alterated 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 (Ibarra, 2015).

5. CONCLUSIONS

The study of hand samples and polished thin-sections allowed identifying different degrees of hydrothermal alteration. It was possible to recognize that the hydrothermal alteration in the SHI is more intense than in the regional rocks. This alteration appears...
with variable intensity and is characterized firstly by muscovite I and, 
and, by quartz II + muscovite II ± clinochlore. Petrographic and 
SEM-EDS performed in samples from the breccia allowed the 
identification of apatite, monazite and other Th-U-REE phospho-
tes as the principal hosts for REE. Apatite is the most common 
accessory mineral and the amount of REE can be metamorpho-
sically removed from apatite to form other REE-bearing minerals, 
such as monazite, which is commonly found as inclusions in apa-
tite. 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, 
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nite, that implies a W, Ti, Sn, P, Th, U, REE mineralization.

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Figure 5 – REE spectra of the studied samples normalised to the chondrite contents (Eversen et al., 1978).
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 corroborate the results previously published using other methodologies.

Key-words: Borralha, Santa Helena Breccia, Pearson’s correlation coefficients, cluster analysis.

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 Venine breccia. This contribution intends to complement results obtained in previous mineralogical studies from Santa Helena breccia, using statistical tools applied to geochemical data.
• 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 - Fe₂O₃ (r=0.6), Ga (r=0.8), Nb (r=0.6) and Ta (r=0.63) alluding the presence of cassiterite;
• Fe₂O₃ - 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 (Al₂O₃ and K₂O: r=0.82).

Intermediated positive correlation [0<r<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, 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, Yb, Lu), once it has been considered very important to distinguish mineral phases enriched in 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, Sm, Eu, Tb, Ho, Yb, Er, Pr, Sm, Gd, Dy, P₂O₅). 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 breccia, instead of REE phosphates (in stage I) because does not have an affinity with P₂O₅.

The second cluster (Cluster 2) represented by P₂O₅, Th, 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.

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

Caracterização geoquímica da Brecha de Santa Helena (Jazigo de tungstênio 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 outcrops 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 I chloride being more evident when the breccia fragments are of metasedimentary rocks. 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, FeO, AsO3, K2O, 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 distinguish mineralized 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 chamadas brechas (breccias). A brecha mais importante e a única aflorante é a de Santa Helena (SSH). Esta apresenta uma mineralização em tungstênio disseminada em zonas com intensa alteração hidrotermal. Esta alteração hidrotermal caracteriza-se pela associação entre muscovita I e II e quartzo I cloro, sendo mais evidente quando os fragmentos da brecha são do tipo granito, pegmatito e pegmatita. Para caracterização da SSH foi realizado um estudo geoquímico comparativo entre zonas mineralizadas em zonas tectônicas e zonas não mineralizadas. A composição geoquímica mostra que existe aumento das concentrações de MnO, FeO, AsO3, K2O, Ba, Nb, Zr, Sn, W e REE em zonas mineralizadas. O estudo geoquímico da SSH pode ajudar a distinguir zonas de mineralização em tungstênio.

Palavras-chave: Brecha de Santa Helena, mineralização de tungstênio, alteração hidrotermal, zonas mineralizadas, caracterização geoquímica

Introduction
In Portugal, the dominant W and Sn deposits are distributed all through the Central Iberian Zone - CIZ, and Galicia-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 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’s 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.

Mineralogy: Four mineralization stages were previously recognized (Gonçalves et al., 2018 in press; Bobos & Noronha, 2017): stage I - ilm ± cs ː l ± ap ± Th-U-REE phosphates ± ms 1 ± sch 1 ± Fe, Mn chl ± bt ± qtz l; stage II - wlf I and II ± sch II ± Nb-W oxides ± ms II ± Fe chl ± qtz II; stage III - main sulphides ± cs I ± 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 wlf and sch in the fragments; (ii) medium (> 5 to 10 mm) to coarse-grained (> 10 mm) wlf in the cement; and (iii) coarse-grained (> 10 mm) wlf in late qtz veins 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...
Results and discussion

Lithological description

Brecia fragments can correspond to big blocks and, in this case, it is difficult to recognize the brecia 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 veins 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).

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 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(tot), MnO and MgO suggesting the presence of disseminated wolframite (Fe2Mn(WO4)) and chlorite; (ii) K2O and Al2O3 associated with the hydrothermal alteration characterized by a potassic alteration.

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).  

<table>
<thead>
<tr>
<th>Element (% wt)</th>
<th>Mineralized (min)</th>
<th>Barren (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>67.1-76.7</td>
<td>71.1-76.7</td>
</tr>
<tr>
<td>Al2O3</td>
<td>12.3-17.4</td>
<td>13.9-14.45</td>
</tr>
<tr>
<td>FeO</td>
<td>2-4.86</td>
<td>1.9-12.38</td>
</tr>
<tr>
<td>CaO</td>
<td>0.21-1.25</td>
<td>0.49-0.71</td>
</tr>
<tr>
<td>MgO</td>
<td>0.46-1.33</td>
<td>0.25-0.42</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.16-0.29</td>
<td>0.71-0.85</td>
</tr>
<tr>
<td>K2O</td>
<td>3.71-9.86</td>
<td>3.43-4.73</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.6-1.71</td>
<td>0.12-0.21</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05-0.19</td>
<td>0.03-0.04</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.12-0.61</td>
<td>0.35-0.44</td>
</tr>
</tbody>
</table>

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, FeO(tot), MgO, Al2O3, K2O, 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.

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