Journal of Iberian Geology

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--Manuscript Draft--

Manuscript Number:	JIBG-D-17-00012R2
Full Title:	Metallographic and in-situ compositional study on columbite-tantalite mining concentrates from placers at Maçainhas (Central-East Portugal): insights for tantalum exploration
Article Type:	Research paper
Funding Information:	FCT (FCT UID/GEO/04683/2013) — Dr. Antonio Moura
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In the middle part of 20th century, the Portuguese Gaia-Maçainhas Sn-Ti-Ta placers were important tin and tantalum producers in Europe. The objective of this work was to recognize the mineralogy of ore concentrates containing colombotantalites, as well as to characterize the textural relations of the different minerals, in order to understand the metallogeny of the primary mineralization. We used reflection microscopy and scanning electron microscopy with X-ray microanalysis (SEM-EDS). Analytical data were validated with electron microprobe analyses in selected grains. The following textures were identified: homogeneous, oscillatory zoning, patchy zoning, irregular mosaic-like intergrowths and biphasic oscillatory zoning. The main compositions identified are columbite-(Mn) and columbite-(Fe), but Fe- and Mn-tantalites are also important minerals as well as ixiolite-wodginite. Most of the minor mineral phases occur as small inclusions in columbite-tantalite and consist of cassiterite, zircon, struverite and microlite group minerals. Results indicate that magmatic-hydrothermal processes, followed by post-magmatic recrystallization, all contributed to the genesis of the Nb-Ta mineralogy in the source lithologies. These were most probably LCT pegmatites located in granitic country rocks which crop out a few kilometers from the placers.

Keywords: alluvial placers, SEM, columbite-tantalite, mineral inclusions, Portugal.

1. Introduction

Tantalum's unique properties are responsible for its extensive use in electronics (approximately 60% of the global production). This is reflected in a high demand of tantalum due to its growing use in the production of electronic devices (Papp 2015). There are at least 62 minerals that contain tantalum as a main constituent, though the vast majority of the metal coming from mines is obtained from just one group of minerals: the columbite-tantalite group. Other minerals of economic interest are tapiolite (orthorhombic $FeTa_2O_6$), the microlite group, the wodginite group and the ixiolite group. Tin-slag material containing tantalum phases as inclusions or tantalum in the cassiterite structure are the second most important source of tantalum (Shaw *et al*. 2011). Typically, tantalite concentrates contain approximately 30% Ta_2O_5.

Several investigations have recently dealt with columbite-tantalites in pegmatites from the Central region of Portugal (Silva *et al*. 2007; Neiva and Ramos 2010; Ramos, 2000; Neiva *et al*. 2015), but none have addressed the mineralogy of alluvium placers in the region. This study presents the first characterisation of columbite-tantalite minerals from the Portuguese Gaia-Maçainhas Sn-Ti-Ta placers, which were very important sources of Sn- and Ta in Europe in the decades from 1950 to 1970.

The main objectives of the present study are to identify the type and composition of columbite-tantalite minerals in the placers, to determine the composition of mineral inclusions, and to characterize grain-scale textural patterns. We will use this information to discuss the petrogenesis of the columbite-tantalite concentrates.

2. **Geological setting**

2.1. Regional Geology

The Guarda-Belmonte region is located within the Iberian Massif, a complex fragment of the European Variscan Belt, subdivided to several geotectonic zones. The Gaia-Maçainhas area is part of the Central Iberian Zone (Julivert *et al*. 1974; Farias *et al.* 1987) which consists of autochthonous metasediments from the early Paleozoic, rare pre-Variscan granites and various Variscan granitoids (Martinez Catalán *et al*. 2004; Fig. 1). In the Guarda-Belmonte region, the metasediments belong to the schist-metagraywacke complex (Upper Proterozoic -Lower Cambrian), which is mainly composed of pelitic schist with interbedded meta-conglomerates and meta-graywackes (Carrington Da Costa 1950; Rodríguez Alonso *et al*. 2004). Three Variscan deformation phases (D1 to D3) are recognized in the area. Late NE-SW quartz veins and WNW-ESE dikes of mafic rocks are widespread (Fig. 1).

The Gaia-Maçainhas placers mainly contain cassiterite plus ilmenite, with subordinate columbo-tantalite as a coproduct. The Maçainhas' stream flows along a NNE-SSW fault, parallel to the currently active late-Variscan Manteigas-Vilariça-Bragança fault zone. It also flows along a set of subparallel normal faults that divide the region in successively dipping blocks.

The geology of the headwater of the stream includes the coarse- to very coarse-grained porphyritic biotite > muscovite Guarda granite (304.1 ± 3.9 Ma), the coarse-grained porphyritic biotite > muscovite Pega granite (301.1 ± 2.2 Ma) and medium-to-coarse-grained muscovite > biotite Fráguas-Pena Lobo granite (299 ± 3 Ma), (Ramos 2010; U-Pb dating from Neiva and Ramos 2010; Neiva *et al*. 2011). The Guarda and Pega granites are late-D3, and the Fráguas-Pena Lobo granite is post-D3. All granites are peraluminous (molecular [Al_2O_3/(Ca0+Na_2O+K_2O)] > 1) and have Nb/Ta ratios lower than 5 (Neiva and

Ramos, 2010) indicating that they are potentially mineralized granites (Ballouard *et al.* 2016).

Granitic aplite-pegmatite sills intrude the three granites as well as the host schist-metagraywacke lithologies, causing contact metasomatism. Emplacement of the sills was influenced by late NNE-SSW and NE-SW trending sub-horizontal fractures (Ramos 2007; 2010).

Various aplite-pegmatite veins and sills were studied in several zones such as the Arcozelo da Serra-Gouveia area (Neiva *et al*. 2008), Pega-Sabugal area (Neiva *et al*. 2012) and Gonçalo-Seixo Amarelo area (Ramos 1998; 2000; 2007; 2010; Neiva and Ramos 2010). The aplite-pegmatite sills belong to the lepidolite and amblygonite subtypes, from the complex type of the LCT (Li-Cs-Ta) family of the rare-element class of pegmatites (Černý and Ercit 2005). The sills from Gonçalo-Seixo Amarelo, which are currently exploited for feldspar and Li, range in width from a few centimeters to 15 m in the amblygonite-subtype, and up to 5 m in the lepidolite subtype (Neiva and Ramos 2010), reaching average grades of 100-150 g Ta per ton (Parra and Filipe 2001). The closest sills and veins to the Maçainhas placer are to the NE of the placer and have not yet been studied in detail regarding their rare minerals potential.

2.2. Historical importance of mining in the area

From 1912 to 1983, several mines exploited the alluvial Sn-Ti-Ta placers in the Gaia-Maçainhas area. The area was named after two small villages located around 25 km south of Guarda city, located in the central part of Portugal. Until 1953, tantalum minerals were unnoticed and sold with the Sn concentrates, mainly to the USA (Soares Carneiro 1959). From 1953 to 1983 the mines produced separate concentrates of Sn, Ti and Ta. The tonnage of columbite-tantalite concentrates represents 5% of the cassiterite concentrates, whereas the quantities of ilmenite concentrates represent 172% of tin concentrates (Parra and Filipe, 2001). The correlations between the quantities extracted of three types of ore concentrates for several of the most important mines in these placers are given in Figure 2. This region was considered to be one of the most productive for tin and tantalum in Europe between 1953 and 1968; e.g., grades (of 2-4 kg Sn/ton and 60-200 g Ta/ton) were among the highest in the world. The alluvial gravel placers were 3-7 m thick and were covered by 1-2 m soil and clay (Parra and Filipe 2001). The bedrock surface was irregular and composed of the granitic country rock. Between 1970 and 1983 the exploitation grade was around 190 g/ton Sn and 10 g/ton Ta-Nb minerals (Parra and Filipe 2001). According to these authors, the production of Ta concentrates diminished with time from 57 tons (1953-1958) to 12 tons (1959-1970) and 2.5-8.5 tons (1971-1983). During the period 1959-1970, the Portuguese Ta production represented around 3% of the world production (396 ton in 1969, according to Kelly and Matos 2013). The Gaia-Maçainhas placers were the most important Sn-Ta mines of Continental Europe (Soares Carneiro 1971) and during the 1960's, previously subeconomic material was exploited. Grades of this material were around 141 g Sn/m^3 (Misk 1972).

3. Methods

A polished section with seventy-three grains obtained from a columbite-tantalite mining concentrate was studied by reflected light microscopy in order to identify zones with different reflectance and/or inclusions of other phases. The SEM-EDS study was performed using a High-Resolution Scanning Electron Microscope with and Energy Dispersive Spectroscopy for X-Ray microanalysis (JEOL JSM 6301F/ Oxford INCA Energy 350) at the Materials Centre of the University of Porto (CEMUP), Portugal. Samples were coated with a carbon thin film, by vapor deposition, using the JEOL JEE–4X Vacuum Evaporator equipment. The images and spectra were obtained at an accelerating voltage of 25 kV and a beam size of 15 µm. Standard deviations (sigma values) for the analysis of Ta, Nb, Fe, Mn, Sn, Ti, Ca, Na were between 1.2 and 0.2%.

Analyses carried out by SEM-EDS yield comparable results to analyses obtained using electron microprobe (Reed 2005), for major elements (Ta, Nb, Fe, Mn) and some minor elements (Ti, Sn, W, Zr). Three points in columbite-tantalite, two in ixiolite-wodginite and three in microlite were analysed using a Hyperprobe Jeol-8500F electron microprobe, equipped with one energy dispersive (EDS) and five wave-length dispersive (WDS) spectrometers, operating at 15 kV accelerating voltage and 20 nA beam current, at the National Laboratory of Energy and Geology (LNEG, Portugal). High correlations were obtained for Ta_2O_5, Nb_2O_5, FeO, MnO, SnO_2, TiO_2, CaO, Na_2O, PbO and UO_2. The following relative errors (EPMA-SEM) were obtained: Ta_2O_5 [0.2, 2.4], n = 7; Nb_2O_5 [0.3, 4.2], n = 8; MnO [0.1, 1.0], n = 5; FeO [0.4, 2.1], n = 4 and TiO_2 [0.03, 2.23], n = 4. Nevertheless, analyses should be considered semi-quantitative, particularly those in phases such as microlite that could have O^{2-}, OH^-, H_2O and vacancies. Only oxides with > 0.1% abundance were considered as representative.

4. Results

Twenty-three grains containing mineral inclusions were identified using the reflected light microscope. Twenty-four zoned grains and eleven homogeneous grains were identified using SEM. We analysed 71 spots or areas from the 73 grains. Ribeiro (2015) analysed 66 spots from 36 other grains. Fernandes (2016) analysed 25 spots from 11 grains (Fig. 3). The data from these two studies were obtained in the same conditions as we have worked (see "methods section"). Four Nb-Ta oxides were observed: columbite group minerals, ixiolite–

wodginite family minerals, microlite subgroup minerals, struverite and cassiterite. Other mineral phases included in the Nb-Ta oxides are also described.

4.1. Grain compositions

Columbite-tantalite is the most widespread Nb-Ta phase. It mainly occurs as discrete grains but, in one case, it occurs as an inclusion within cassiterite. Compositions plot within in the columbite-(Fe), columbite-(Mn), tantalite-(Fe) and tantalite-(Mn) fields (Fig. 3). In these minerals, major elements show large variations: 9.2 to 61.5 wt.% Ta_2O_5 (average 45.4 wt.%), 21.6 to 70 wt.% Nb_2O_5, (av. 34.5 wt.%), 0.0 to 14.4 wt.% FeO (av. 9.7 wt.%) and 4.4 to 18.5 wt.% MnO (av. 9.8 wt.%). Minor elements vary from <0.1 to 2.3 wt.% (TiO_2 average 1.22 wt.% for 23 points analysed; only one analysis had detectable SnO_2, at 1.8 wt.%). Mn/Fe and Ta/Nb ratios show large variations: Mn/(Mn+Fe) = 0.25-1.0 and Ta/(Ta+Nb) = 0.08-0.63. Ixiolite $(Ta,Mn,Nb)O_2$ and wodginite (Mn^{2+},$Sn^{4+}Ta_2O_8$) are also plotted in Figure 3. These Sn-rich minerals exhibit the following compositions: 64.2-55.5 wt.% Ta_2O_5 (av. 59.5 wt.%), 14.5-6.0 wt.% Nb_2O_5 (av. 11.5 wt.%), 10.9-4.7 wt.% FeO (av. 7.7 wt.%), 9.5-4.1 wt.% MnO (av. 7.1 wt.%), 7.55 to13.62 wt.% SnO_2 (av. 11.0 wt.%), 1.26 to 7.32 wt.% TiO_2 (av. 3.4 wt.%), and Mn/(Mn+Fe) = 0.28–0.67 and Ta/(Ta+Nb)= 0.70–0.87. Representative compositions are given in Table 1.

4.2. Types of zoning

Columbite-tantalite and ixiolite-wodginite minerals show different types of zoning. We observed two of the three simple types described by Lahti (1987): oscillatory and patchy zoning. We further distinguished more complex textures such as rhythmic (biphasic) regular oscillatory zoning and irregular mosaic-like intergrowths.

The oscillatory zoning is the most common. Sharp contacts are rare and smooth, gradual transitions dominate. Figure 4a shows an example of coarse regular oscillatory zoning, where the compositions vary from columbite-(Mn) to tantalite-(Fe). In its turn, Figure 4b is an example of fine regular oscillatory zoning. Figures 4c and 4d show a compositional transverse in a regular oscillatory zoned crystal, where Nb and Ta concentrations mirror each other. Irregular oscillatory zoning is evident in Figure 5a and expressed by the occurrence of zones with higher Nb and Fe contents (darker zones). Patchy zoning and reverse zoning are present in a few grains (Figs. 5b and 5c). An example of irregular mosaic-like intergrowths of columbite-(Mn) and ixiolite-wodginite is shown in Fig. 5d. Rhythmic (biphasic) regular oscillatory zoning (Fig. 6) describes a rhythmic oscillation zonation between ixiolite-wodginite in lighter zones and tantalite-(Fe) or tantalite-(Mn) in darker zones.

4.3 Mineral inclusions

Columbite-Tantalite grains often show mineral inclusions, which can be enriched or depleted in Nb-Ta (Table 2). Among the first ones are Nb- and Ta-bearing cassiterite (SnO_2), struverite [$(Ti,Ta,Fe)O_2$] and microlite group minerals. Among the latter are zircon ($ZrSiO_4$) and Nb- and Ta-free cassiterite. These inclusions show different textural relations with the host grains.

Cassiterite occurs as a separate phase (primary individual grains, Fig. 7a) in columbite-tantalite. It shows a fainted grey color under reflect light, may be anhedral to euhedral, with grain dimensions ranging from 9 to 28 μm. It also occurs as inclusions in columbite-(Fe), tantalite-(Fe) and ixiolite-wodginite minerals. Cassiterite may include up to 8% of Nb and Ta in its crystal structure.

Zircon is characterized by a darker grey color in reflected light and has anhedral to suhedral habit in grains that vary in size from 18 to 46 μm. It occurs in columbite-(Fe) and columbite-(Mn) only as individual grains (Fig. 7b).

Struverite is white under reflected light and occurs included in columbite-(Fe). It may occur as individual anhedral or subhedral grains that range in dimension from 3 to 41μm (Fig. 7a and b) or as zoned microveinlets. The irregular zoning is due to small variations in Nb and Ta. Compositionally, Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios range from 0-0.07 and from 0.65-0.82, respectively.

At least two different microlite phases are present (Table 2). The F-bearing phase forms anhedral irregular mosaic intergrowths with columbite-(Mn) and ixiolite-wodginite and the Pb-bearing phase was only observed included in tantalite-(Fe) reaching 22 μm across (Fig. 7c). Both have light grey color under reflected light and appear to be the result of post-magmatic events.

A single subhedral columbite-(Mn) grain (about 20 μm across) was also observed included in a cassiterite grain.

5. Discussion and conclusions

Figure 2 shows the correlations between the three main mineral-commodities recovered from the alluvial concentrates. Ilmenite and cassiterite correlate well due to presence of S-type granites (Ti source) and aplite-pegmatites (Sn source). Columbite-tantalite and ilmenite correlation is relatively poor because columbite-tantalite is a scarce mineral in the primary source. However, the correlation between columbite-tantalite and cassiterite is moderate because both minerals are presumably derived the same pegmatitic source.

In the columbites-tantalites from Maçainhas placer, Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios (also described as #Mn and #Ta) vary from 0.25 to 1 and from 0.08 to 0.63, respectively. Minor elements are present in quantities that range from <0.1 to 4.16 wt.% TiO_2 and from <0.1 to 2.17 wt.% SnO_2 (Fig. 8). The values of WO_3 were always below 0.1 wt.% except in one grain reaching 0.84 and 2.82 wt % WO_3.

Melcher *et al*. (2015) calculated a 'global median' for trace elements and Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios of columbite group minerals using data from 29 ore provinces around the world. Figure 8 allows a comparison between the SnO_2 and TiO_2 contents of the present study and the values obtained in the previously referred 'global median'. SnO_2 and TiO_2 contents of Maçainhas' columbite-tantalites reach higher values than those of the 'global median'. However, when only one of these minor elements is present, its content is lower than the 25th percentile calculated by Melcher *et al*. (2015). Due to the scatter of the data in the diagram of Figure 8, we conclude that there is no correlation between SnO_2 and TiO_2. Both Mn/Fe and Ta/Nb ratios for the columbite-tantalite minerals of Maçainhas, range from values lower than the 25th percentile to values that outcome the 75th percentile calculated in the 'global median'.

This wide range in ratios indicate a large compositional variation, that may be the result of a mixture of columbite-tantalite grains from different aplite-pegmatite sills and veins that intruded the country rock granites drained by the Maçainhas stream.

The TiO_2 and SnO_2 contents of columbite-tantalite minerals are 0.05-2.3 wt. % and 0.05-0.80 wt. % in the Gonçalo area, respectively (Neiva and Ramos 2010), and range from 0.86 to 4.03 wt. % TiO_2 and from 0.06 to 0.7 wt. % SnO_2 in the Cabeço dos Poupos, Pena de Lobo–Sabugal zone (Neiva *et al.* 2011).

The TiO_2 content and its variation is similar to other columbite-tantalites studied in the region (Neiva and Ramos 2010; Neiva *et al.* 2011). However, the SnO_2 content is higher than those reported in the region. Similar contents were described in the Central French Massif, reaching 1.37 wt. % of SnO_2 (Belkasmi and Cuney 1998).

The quadrilateral diagram of Figure 3 is of potential use to pin-point pegmatite types using columbite group mineral compositions, particularly in those cases where associated minerals (e.g. major silicates and phosphates) do not exist, as is this case of alluvial placer deposits (Melcher et al., 2016). Accordingly, the results of this study coupled with data from literature strongly suggest that these columbite group minerals come from LCT pegmatites not yet found.

Compositional variation of columbite-tantalite obtained from aplite-pegmatites sills and veins of the region, are similar to columbite-tantalite from Li-rich and Be-rich aplite-pegmatite sills and veins and pegmatite veins that intruded the Pega's granite (Ramos *et al.* 2006; Neiva *et al.* 2012). Importantly, columbite-tantalite compositions are similar those from Li-rich sills of the Gonçalo Li mine, and the pegmatite field west of Gaia placers (Ramos *et al.* 2006; Neiva and Ramos 2010).

However, in view of the geomorphology of the region and the fact that it experienced similar erosion rates during the Quaternary, none of the previously studied sills and veins could have contributed with columbite-tantalite grains to the placer of Maçainhas, since there are many topographic obstacles, such as ridge lines and streams valleys, separating them. Therefore, columbite-tantalite from the Maçainhas placer must have been sourced from the erosion of undiscovered LCT pegmatites veins and sills located to the northeast of the placer. This suggests that the region has considerable potential for further exploration.

The ixiolites-wodginites from Maçainhas placer have Mn/(Mn+Fe) and Ta/(Ta+Nb) ratios ranging from 0.28 to 0.67 and from 0.70 to 0.87, respectively. Minor elements are present in quantities that range from 1.26 to 7.32 wt. % TiO_2 and from 7.55 to 13.62 wt. % SnO_2. According to Melcher *et al*. (2016) using data of wodginite–ixiolite collected in 18 ore provinces, the median of Mn/Fe ratio is 0.66, whereas Ta/Nb commonly ranges from 0.65 to 0.95. The SnO_2 concentrations range from 0.1 to 33 wt.%, with an average and median of 12 wt.%. The concentrations of TiO_2 can go up to 21 wt.%, while the median is 1.60 wt.%. Thus except for Mn/Fe, data from the Maçainhas placer are similar to those obtained by Melcher *et al*. (2016). The Mn/Fe ratio range between values lower than the median. This could indicate that Mn-Fe substitution is not complete (Melcher *et al*. 2016).

Textural patterns provide important information about the formation of Nb-Ta phases. Zoning is due to variations in the major elements, mainly in Ta and Nb. Lahti (1987) considered that the main factors controlling oscillatory zoning are the growth dynamics of the crystals, particularly the rates of concentration and diffusion of the main elements, and the successive flows of the magmatic fluid in an intrusion channel. In other words, zoning reflects a non-equilibrium fractional crystallization from the parent material caused by the slow diffusion of Nb and Ta in the melt relative to the crystal growth rates.

As crystals grow, they locally evolve to Ta-Mn-rich compositions and, when the growth periodically stops (due to depletion of components) or when the crystal growth projections overcome the boundary layer into fresh bulk liquid, they may return to Nb-rich compositions (Neiva *et al.* 2008). This type of zoning is often interpreted as a primary magmatic feature (e.g. Lahti 1987; Van Lichtervelde *et al.* 2007). Gradual contacts indicate a diffuse re-equilibrium, while sharp contacts indicate the opposite, reflecting the absence of re-equilibrium caused by an interruption, followed by a new flux of magma (Linnen and Cuney 2005).

Patchy zoning consists of an irregular zoned phase replacing earlier regular zones (Van Lichtervelde *et al.* 2007). Patchy zoning (Fig. 5b) along with irregular and mosaic textures (Fig. 5d) may indicate non-magmatic, metamorphic or hydrothermal recrystallization, partial leaching, metasomatic replacement or alteration (e.g. Lahti 1987; Černý *et al*. 1992; Badanina *et al.* 2015).

Rhythmic (biphasic) regular oscillatory zoning between ixiolite-wodginite and tantalite (Fig. 6) is due to the mechanism of substitution in which Fe, Mn and Nb are replaced by Sn an Ti, according to: 3 $(\mathrm{Sn,Ti})^{4+} \leftrightarrow (\mathrm{Fe,Mn})^{2+} + 2(\mathrm{Nb})^{5+}$.

Patchy zoning (Fig. 5b) as well as rhythmic (biphasic) zoning (Fig. 6) and irregular mosaic-like intergrowths (Fig. 5d) have not previously been described in any of the studies on columbite-tantalite from aplite-pegmatite veins and sills of the region. Nevertheless, patchy zoning and irregular mosaic-like intergrowths are commonly observed in columbite-tantalite from pegmatites (e.g. Van Lichtervelde *et al.* 2007; Badanina *et al.* 2015) and form placers (Uher *et al.* 2007; Alfonso *et al.* 2015).

Therefore, textural patterns described for columbite-tantalite minerals in this study are interpreted to indicate two main crystallization events: one primary magmatic event responsible for the regular oscillatory zoning (Fig. 4a and b), the biphasic regular oscillatory zoning (Fig. 6) as well as the homogeneous crystals, followed by one post-magmatic recrystallization responsible for the other textures (Fig. 5a to d).

On the basis of textural relations, we interpret the origin of the anhedral irregular mosaic intergrowths with columbite-(Mn), ixiolite-wodginite and microlite to reflect post-magmatic subsolidus partial leaching and subsequent replacement and recrystallization, analogous to those studied by Uher *et al.* (2007). Furthermore, the irregular and patchy zonation is also likely related to this subsolidus overprint.

Cassiterite, zircon and struverite inclusions in columbite-tantalite grains indicate a primary magmatic origin. However, the cross-cut character of struverite zoned microveinlets may also indicate crystallization of this Ta-rutile phase during the subsolidus event., while microlite crystallization appears to be exclusive post-magmatic. The high lead contents of four analyses in this group of minerals suggests an external source (Uher *et al*. 1998).

There is no information regarding mineral inclusions in the sills and veins of the region. However, discrete grains of rutile, zircon, cassiterite and microlite have been reported. Microlites, in the Gonçalo zone, contain similar F contents to those reported in the current study.

Further electron microprobe (EPMA) studies of columbite-tantalite, cassiterite and ilmenite concentrates will provide additional mineralogical data for this and other important placer deposits in the area. Ultimately, the aim will be to constrain the geological processes that controlled the crystallization of the minerals in the primary orebodies and discover the primary mineralisation.

Acknowledgments

We thank Daniela Silva and CEMUP (Materials Centre of the University of Porto) for SEM analysis and semi-quantification of the data. The Portuguese Science Foundation is thanked for financial support through the FCT UID/GEO/04683/2013 project. Ricardo Ribeiro's permission to use the unpublished SEM data from his 2015 work is greatly appreciated. We are deeply grateful to Prof. Ana Neiva, Dr. Paulo Bravo and the two anonymous referees for careful reading the article, which improved the quality of the work. The valuable comments of the handling Editor Teresa Ubide also improved the quality of the manuscript.

Declaration of interest statement

There is no conflict of interest.

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Table 1 Selected grain compositions of Columbite-Tantalite (Col: Columbite; Tant: Tantalite) and Ixiolite-Wodginite (Ixt-wdg.) minerals from the Maçainhas placer (in wt %)

– non detected; Hom. – homogenous; Msc. - mosaic-like; Rthm – rhythmic biphasic; I – irregular; C – coarse. Cation formula based on 6 oxygen atoms

Table 2 Representative compositions of mineral inclusions found in Columbite-Tantalite grains (in wt %)

– non detected. Cation formula based on two oxygen atoms for cassiterite and struverite and sixteen oxygen atoms for Zircon

Fig. 1 Geological map from the Guarda-Belmonte region (central east Portugal). Adapted from the 1:500.000 Portuguese Geological Map (IGM 1995).

Fig. 2 Relative proportions between the exploited concentrates from several of the most important mines in the Guarda-Maçainhas placers (Couto Mineiro da Gaia, Couto Mineiro de Maçainhas, Couto Mineiro de Colmeal, Concessão de Olas, Concessão da Barreira, Concessão da Torre Romana, Porto Sabugal, Bica da Gaia, Salão nº1, Carvalheira e Codiceira, Lameirão, Pimenta, Fonte Jardina and Ginjal). Data collected from Parra and Filipe (2001) and Teixeira et al. (1965)

Fig. 3 Compositions of columbite-tantalite (circles and squares) and ixiolite-wodginite (triangles) plotted in the columbite quadrilateral diagram. In black: data collected during this study; Grey: SEM-EDS data from Ribeiro (2015); Squares: EPMA data from Fernandes (2016). Compositional gap (thin black dashed line) between tapiolite and tantalite taken from Černý et al. (1992). Dotted line: columbite-tantalite compositions from Pega-Sabugal area (Neiva et al., 2011). Thick dashed line: CT compositions from Gonçalo-Seixo Amarelo area (Neiva and Ramos, 2010)

Fig. 4 BSE images of Nb-Ta minerals. Types of zoning: a – Coarse regular oscillatory zoning; b – Fine regular oscillatory zoning; c – Regular zoning with four analysed points oscillating between columbite-(Fe) and columbite-(Mn); d – Graphic representing a compositional transverse across the grain C

Fig. 5a – Irregular oscillatory zoning in columbite-(Mn); b – Patchy zoning with replacement tongues in the rims of the crystal; c – Reverse zoning with tantalite-(Mn) in the core and columbite-(Mn) in the rims; d – Irregular mosaic-like intergrowths of columbite-(Mn). Ixiolite-wodginite and Ta>Nb-rich rutile "struverite" (white areas)

Fig. 6a – BSE image of biphasic regular oscillatory zoning between tantalite and ixiolite-wodginite; b – Compositional traverse across the grain

Fig. 7 Mineral inclusions under reflected light to the left and BSE images of mineral inclusions on the right: a – cassiterite (fainted grey) and struverite (white) in columbite-(fe); b – zircon (dark grey) and struverite (white) in columbite-(Fe); c – intergrowth of columbite-(mn), ixiolite-wodginite (both whitish grey) and microlite (light grey)

Fig. 8 TiO_2 versus SnO_2 of columbite-tantalites from the Maçainhas' placer (data from Ribeiro, 2015). Triangle, square and diamond are values of 25th percentile, median and 75th percentile from 29 columbite-tantalite provinces around the world (Melcher. *et. al*. 2015; Melcher *et al*. 2016)

Table 1

Grain nº	**8**	**13**		**27**		**26**		**36**	**43**	**54**		**58**	
Analysis nº	1b	2	3b	1a	8	2a	6	2	1	1a	2	1a	1b
Mineral	Ixt.-wdg.	Ixt.-wdg	Col-(Mn)	Ixt.-wdg.	Tant-(Fe)	Tant-(Fe)	Col-(Fe)	Col-(Fe)	Tant-(Mn)	Col-(Mn)	Col-(Mn)	Col-(Mn)	Tant-(Fe)
Zoning type	Hom.	Msc. intergrowths		Rthm. oscillatory		Msc. intergrowths		Hom.	Hom.	I. oscillatory		C. oscillatory	
Ta_2O_5	55.55	62.06	45.62	59.70	55.18	55.64	34.83	9.21	60.39	28.48	35.48	14.15	59.10
Nb_2O_5	14.47	7.79	34.80	12.48	25.25	23.28	41.91	66.99	24.42	50.65	46.04	63.69	23.32
SnO_2	8.43	12.00	–	11.75	–	–	–	–	–	–	–	–	–
TiO_2	5.26	5.27	1.37	1.51	1.71	3.06	3.01	2.29	–	–	–	–	–
FeO	10.86	4.70	3.45	7.54	9.28	12.77	14.44	13.39	–	9.74	0.00	7.93	8.95
MnO	5.43	8.17	14.77	7.03	8.58	5.24	5.82	8.12	15.20	11.13	18.48	14.24	8.63
Total	100.00	99.99	100.01	100.01	100.00	99.99	100.01	100.00	100.01	100.00	100.00	100.01	100.00
Ta	1.466	1.702	0.848	1.653	1.076	1.083	0.614	0.145	1.209	0.493	0.631	0.230	1.186
Nb	0.635	0.355	1.075	0.574	0.819	0.753	1.228	1.756	0.812	1.459	1.360	1.723	0.778
Sn	0.326	0.482	–	0.477	0.000	–	–	–	–	–	–	–	–
Ti	0.384	0.400	0.070	0.116	0.092	0.165	0.147	0.100	–	–	–	–	–
Fe	0.881	0.396	0.197	0.642	0.557	0.764	0.783	0.649	–	0.519	–	0.397	0.552
Mn	0.446	0.698	0.855	0.606	0.521	0.318	0.319	0.399	0.947	0.601	1.023	0.722	0.539
Total	4.138	4.033	3.045	4.068	3.065	3.083	3.091	3.049	2.968	3.072	3.014	3.072	3.055
Mn/(Fe+Mn)	33.6	63.8	81.3	48.6	48.3	29.4	28.9	38.1	100.0	53.7	100.0	64.5	49.4
Ta/(Ta +Nb)	69.8	82.7	44.1	74.2	56.8	59.0	33.3	7.6	59.8	25.3	31.7	11.8	60.4

Grain nº	13		26		2	27	22	54	12	56
Analysis nº	1b	1d	1a	4a	3	1b	1	1b	4	1
Mineral	Microlite		Microlite		Cassiterite		Zircon		Struverite	
Ta_2O_5	75.52	72.72	54.77	47.95	3.10	10.83	–	–	32.27	7.83
Nb_2O_5	5.55	6.39	24.49	19.76	–	–	–	–	10.62	11.48
SnO_2	–	–		–	95.55	87.76	–	–	2.49	–
TiO_2	–	–	3.12	3.31	–	–	–	–	43.20	75.31
FeO	–	–	6.82	1.70	1.35	1.40	–	2.05	10.66	5.31
MnO	–	–	9.04	–	–	–	–	–	0.76	–
CaO	9.77	8.53	1.77	2.41	–	–	–	–	–	–
Na_2O	4.35	3.25	–	–	–	–	–	–	–	–
PbO	–	–	–	24.87	–	–	–	–	–	–
UO_3	–	4.82	–	–	–	–	–	–	–	–
ZrO_2	–	–	–	–	–	–	59.96	68.80	–	–
SiO_2	–	–	–	–	–	–	26.56	29.15	–	–
HfO_2	–	–	–	–	–	–	13.48	–	–	–
F	4.81	4.82	–	–	–	–	–	–	–	–
	102.02	101.79								
O≡F	2.02	1.80								
Total	97.98	98.19	100.01	100.00	100.00	99.99	100.00	100.00	100.00	99.99
Ta	1.782	1.745	1.052	1.066	0.021	0.075	–	–	0.159	0.134
Nb	0.218	0.255	0.782	0.730	–	–	–	–	0.087	0.038
Ti	–	–	0.166	0.204	–	–	–	–	0.588	0.729
Sn	–	–	–	–	0.959	0.891	–	–	0.018	–
Zr	–	–	–	–	–	–	4.22	4.222	–	–
Si	–	–	–	–	–	–	3.670	3.670	–	–
Hf	–	–	–	–	–	–	0.516	–	–	–
Fe	–	–	0.403	0.116	0.028	0.030	–	0.216	0.161	0.114
Mn	–	–	0.541	–	–	–	–	–	0.012	0.134
Ca	0.908	0.806	0.134	0.211	–	–	–	–	–	–
Na	0.825	0.627	–	–	–	–	–	–	–	–
Pb	–	–	–	0.547	–	–	–	–	–	–
U	–	0.089	–		–	–	–	–	–	–
				Total	1.008	0.996	7.484	8.000	1.025	1.015

Figure 1

Click here to download Figure Fig1.jpg

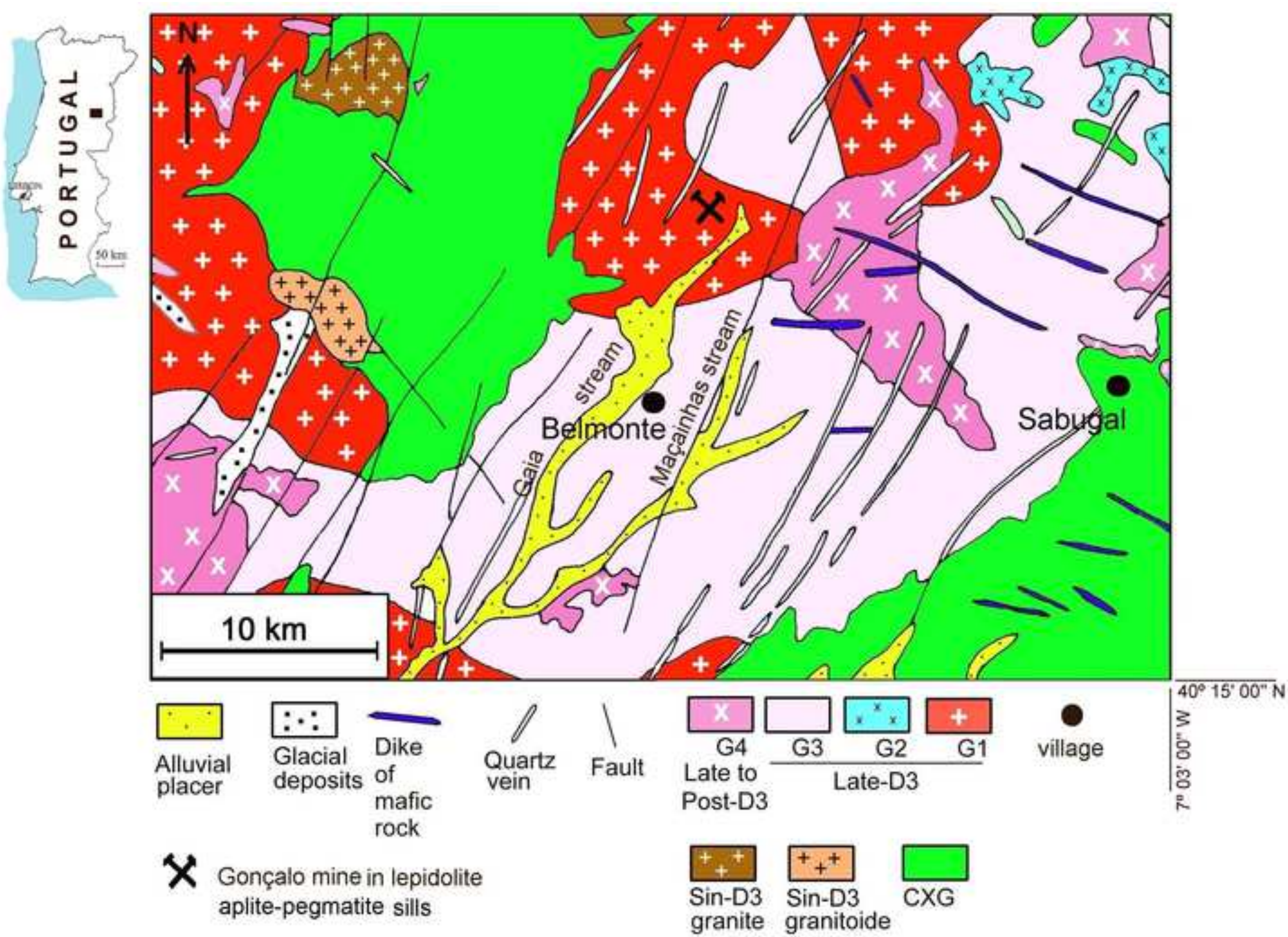

Figure 2

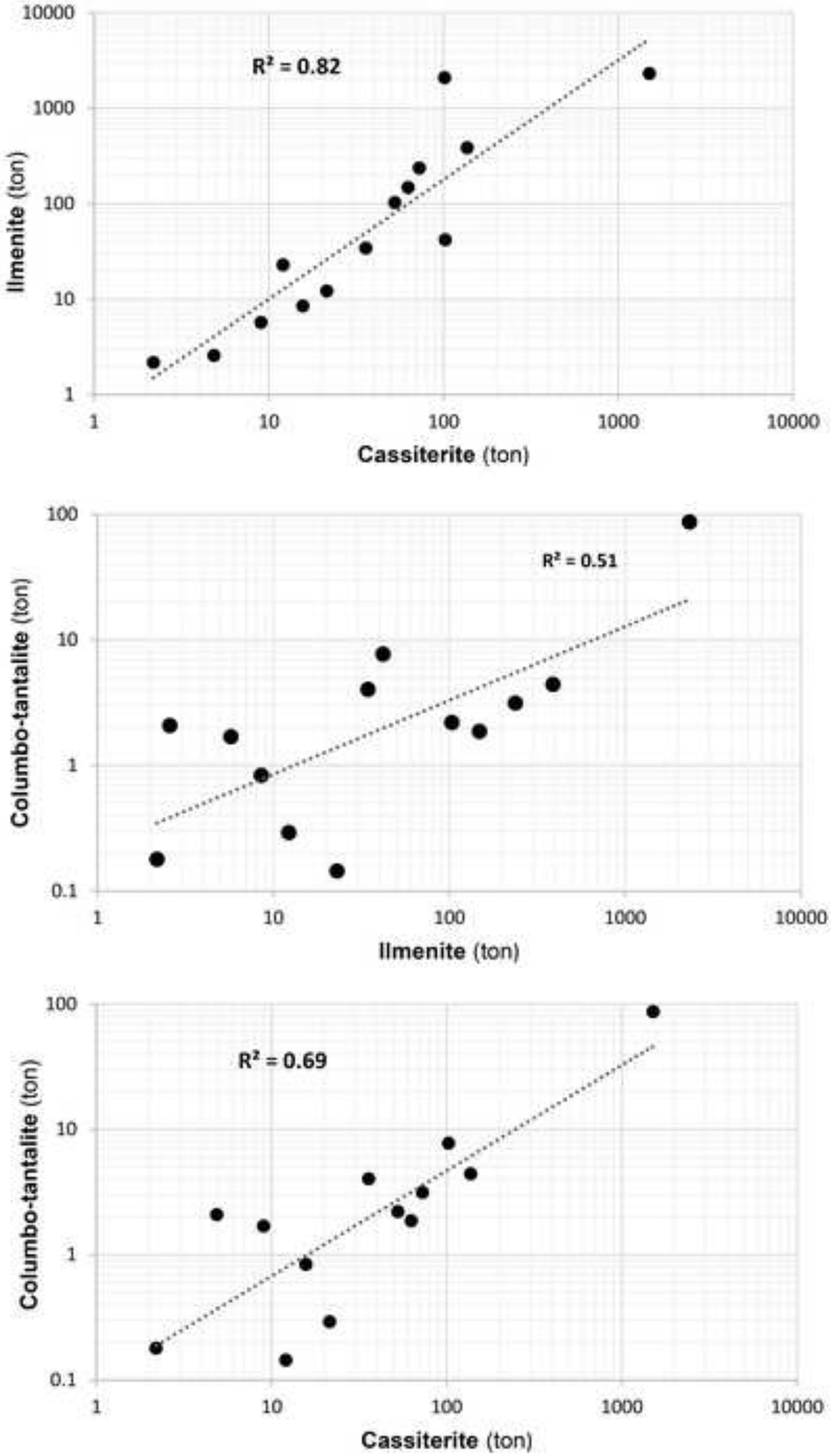
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Figure 3

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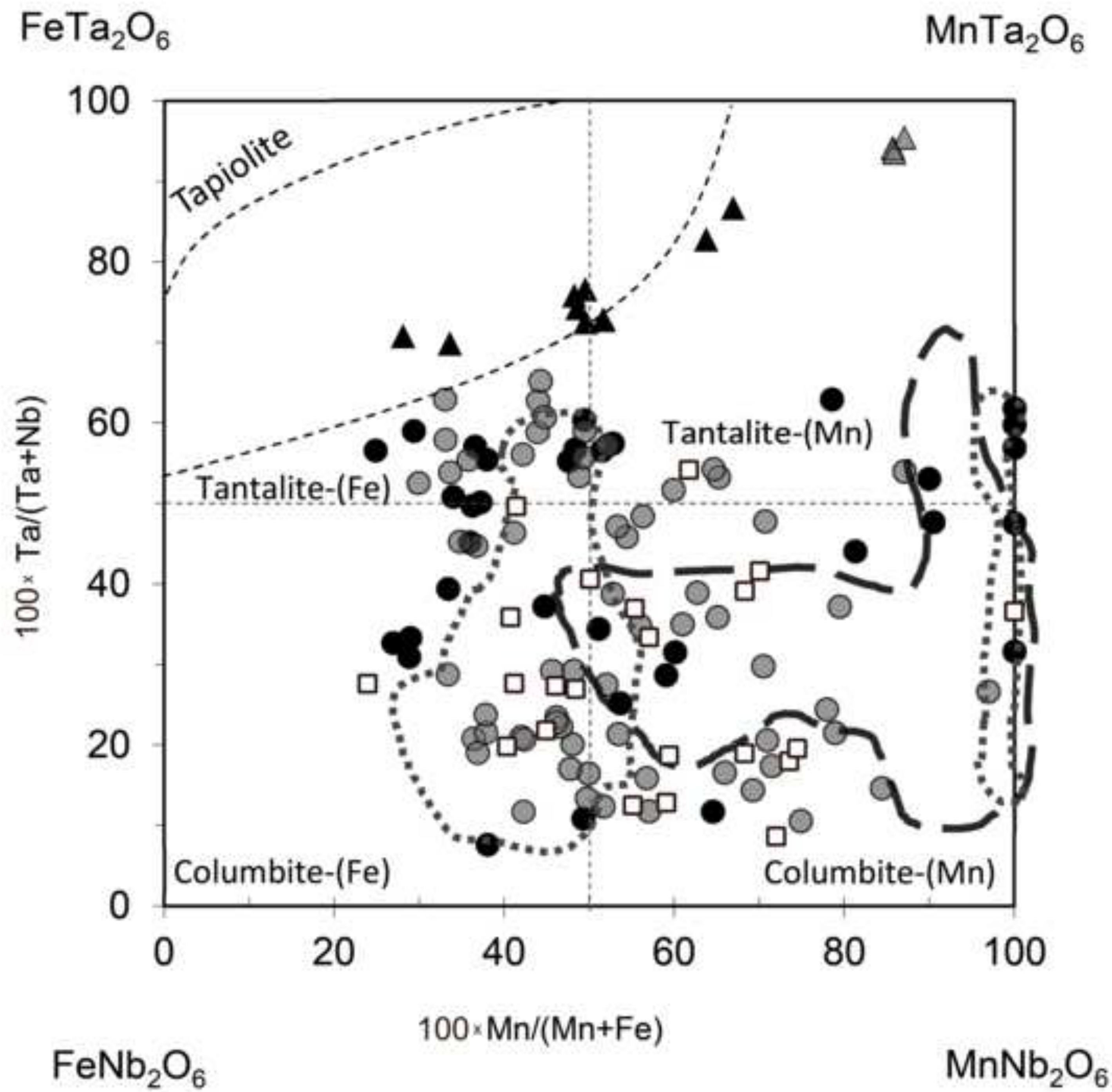

Figure 4

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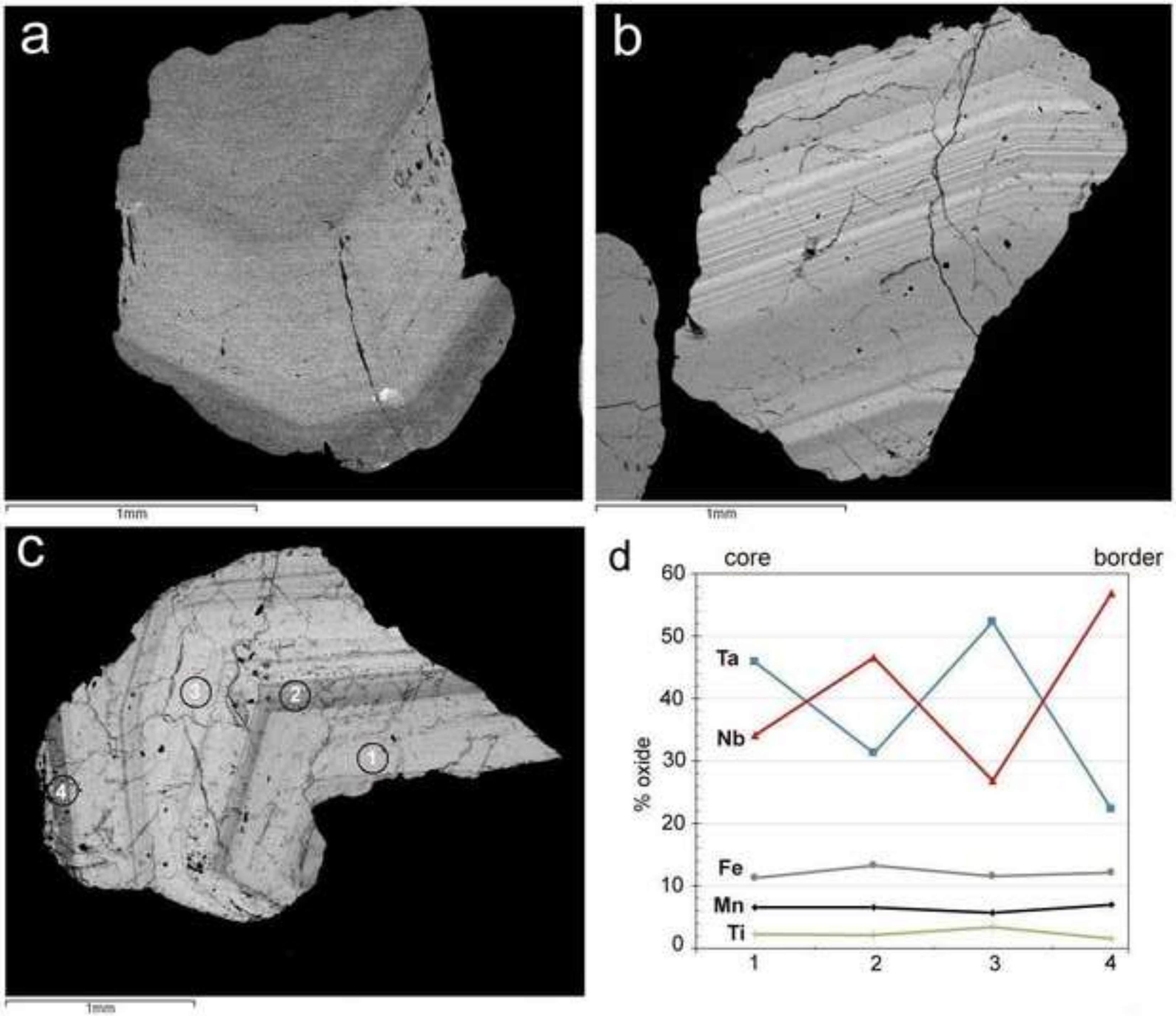

Figure 5

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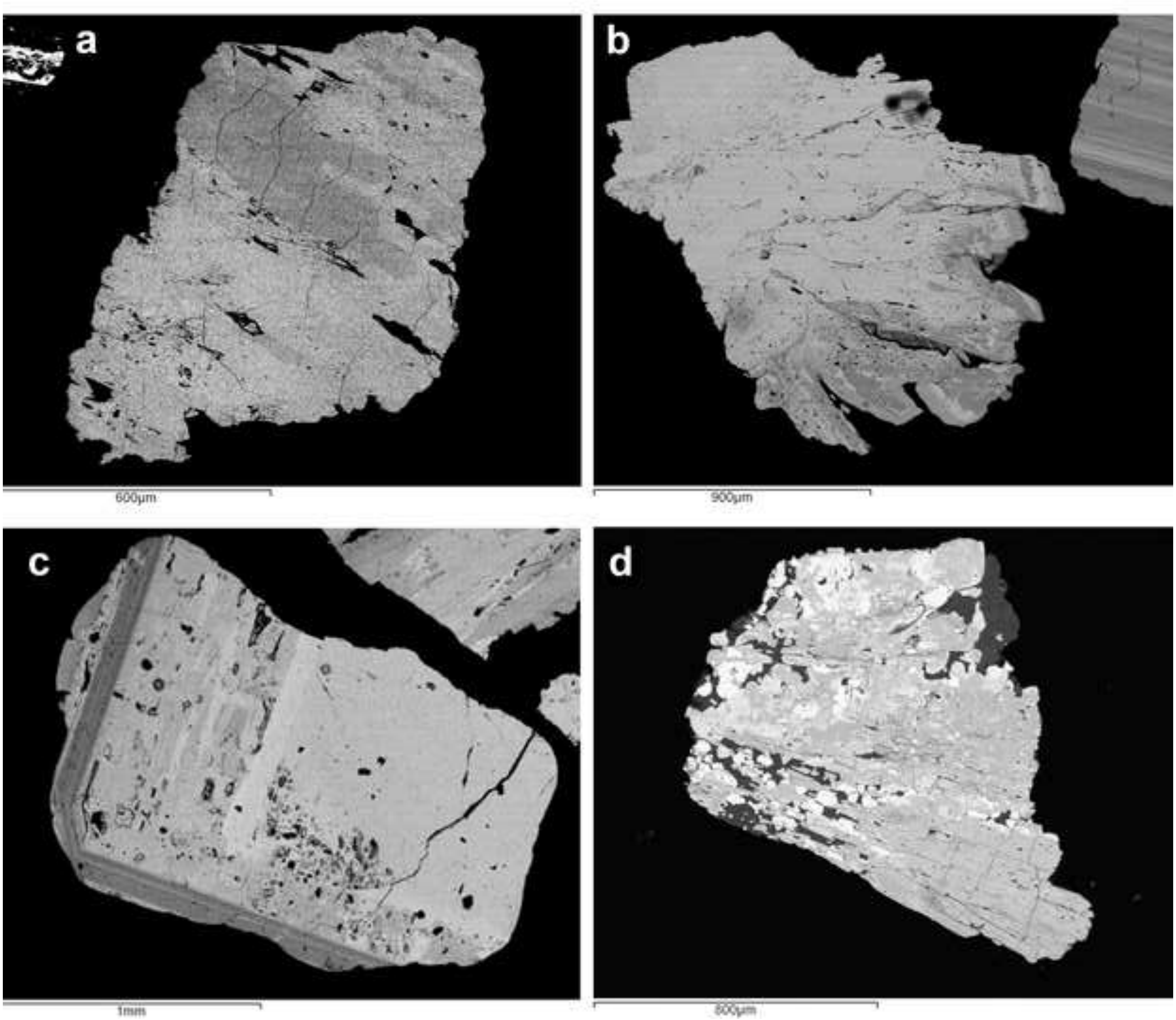

Figure 6

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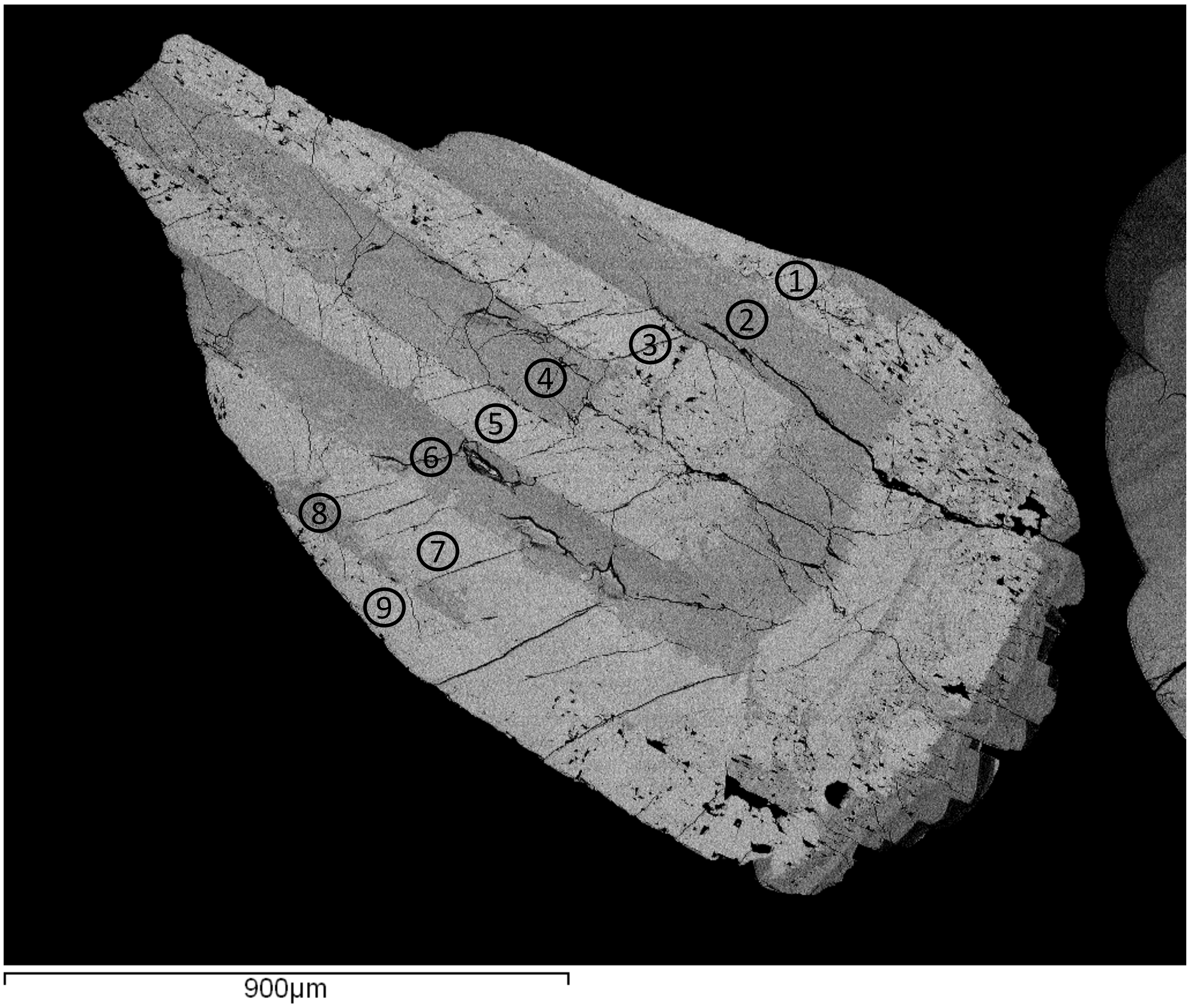

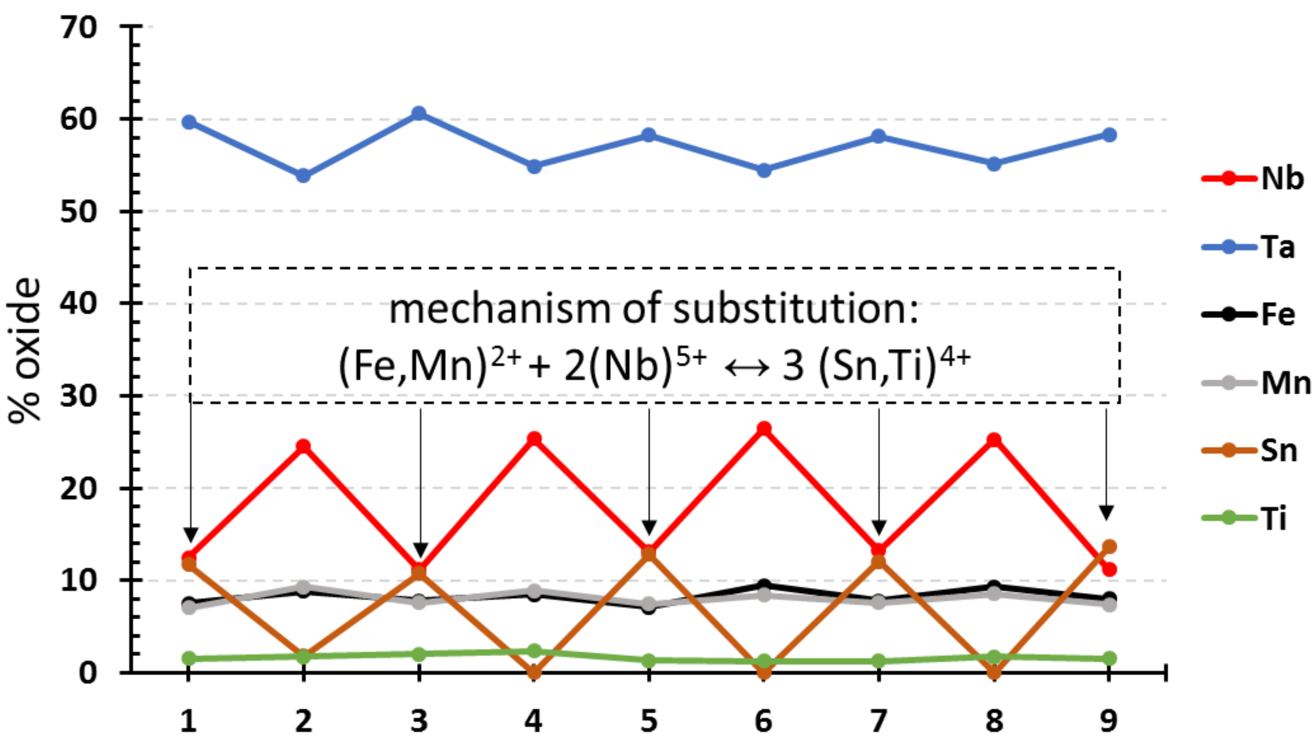

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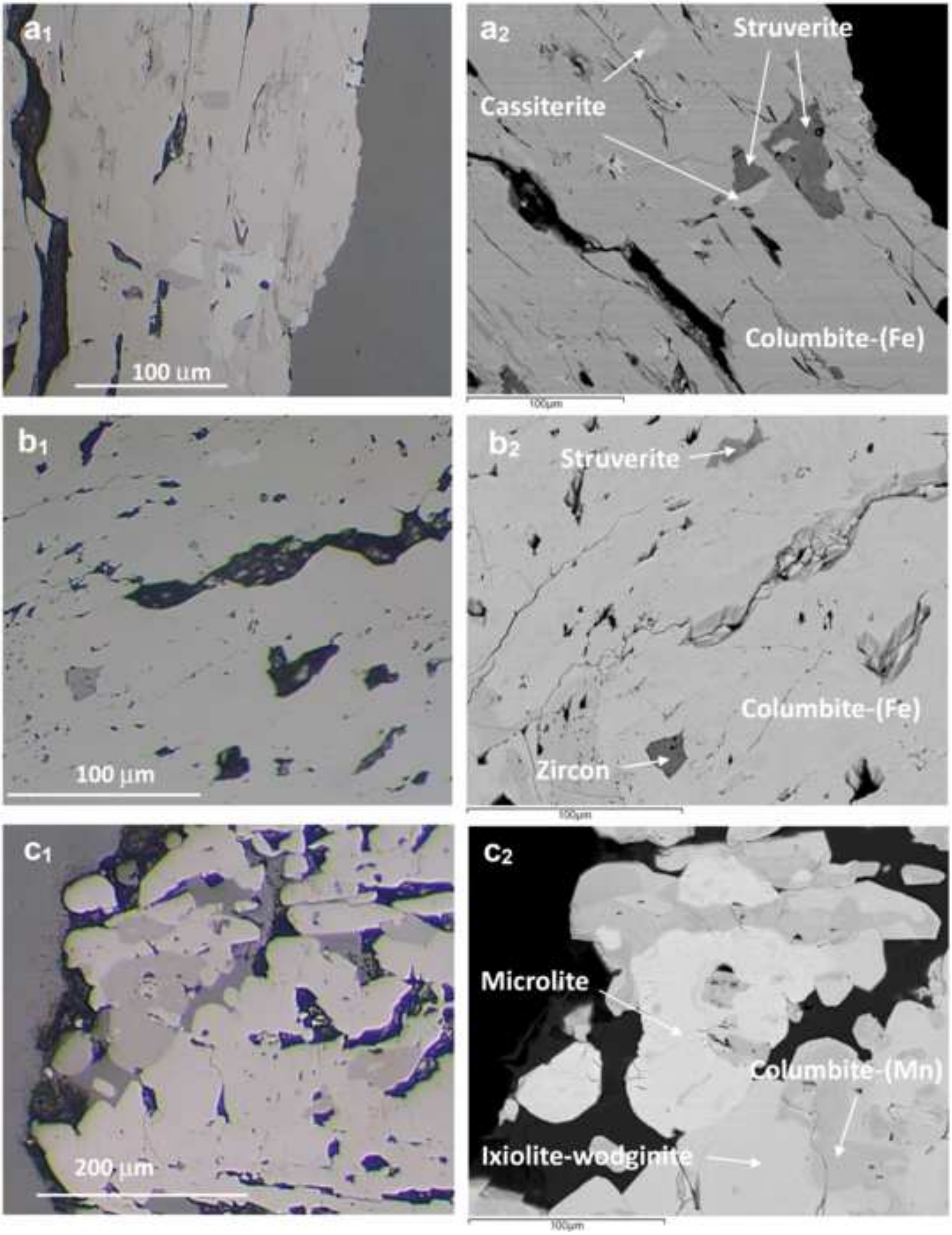
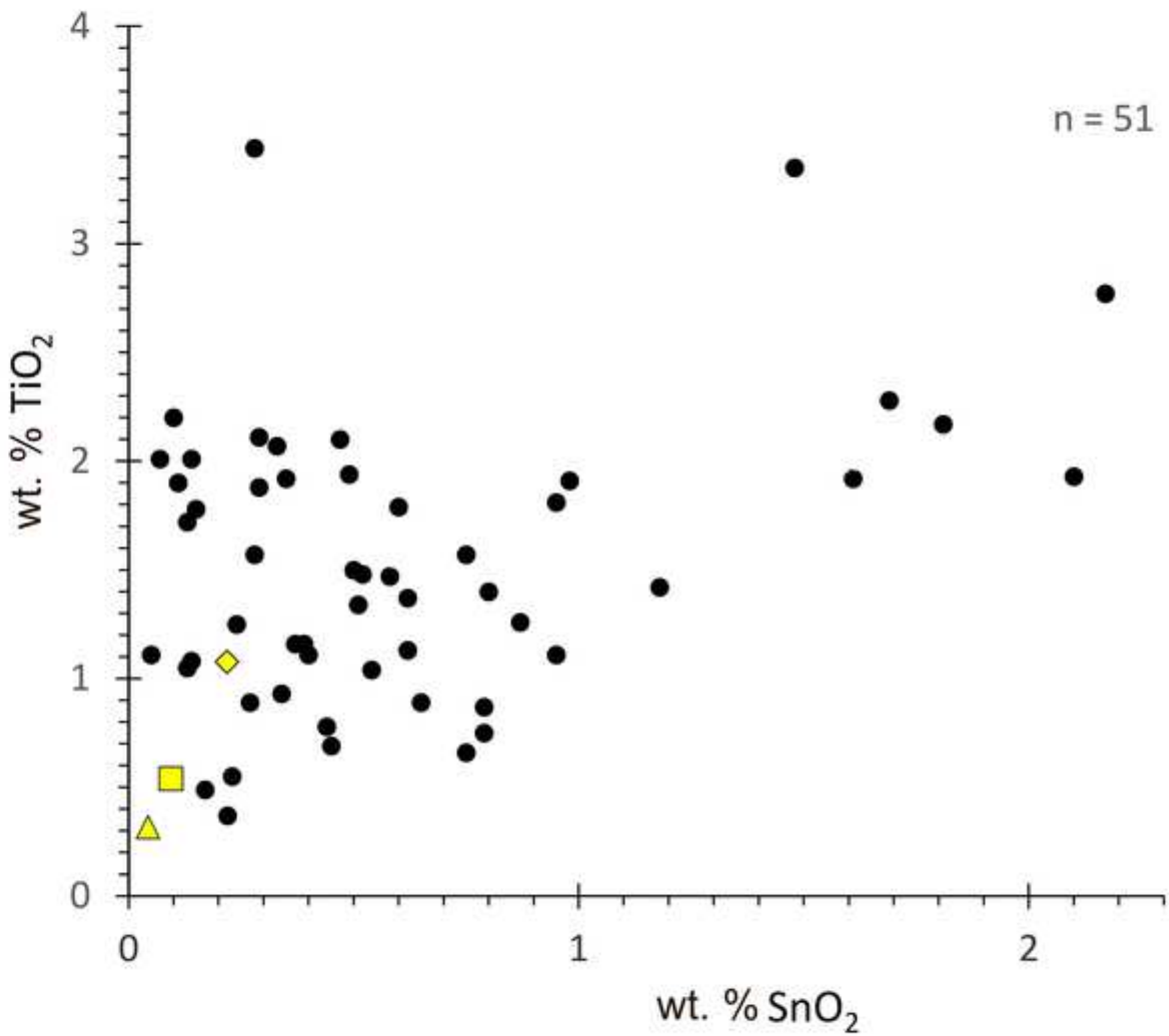


Figure 8



Response to comments and suggestions to the article JIBG-D-17-00012:

We deeply thank the corrections and comments made.

Title

We accept the suggestion for the title but we would prefer to switch Nb-Ta for tantalum, although it is not a mandatory change:

1

Metallographic and in-situ compositional study on columbite-tantalite mining concentrates from placers at Maçainhas (Central-East Portugal): insights for tantalum exploration in the area

Justification:

Columbotantalites are the main mineral for tantalum production. Niobium are almost exclusively obtained from pyrochlore rich-ores in carbonatites and/or alkaline igneous rocks and associated laterites. For this reason, we suggest that Tantalum is more appropriated then Nb-Ta, in the title.

Abstract

These were most probably LCT pegmatites located in granitic country rocks which crop out a few kilometers from the placers.

We suggest that we do not need to explain this in this ABSTRACT section, but we explain it later in page 5 (please see next comment)

Page 5

The aplite-pegmatite sills belong to the rare-element class LCT family, complex type as well as lepidolite and amblygonite subtypes (Černý and Ercit 2005).

We have rewritten the phrase:

2

The aplite-pegmatite sills belong to the lepidolite and amblygonite subtypes, from the complex type of the LCT (Li-Cs-Ta) family of the rare-element class of pegmatites (Černý and Ercit 2005).

Page 7

Ribeiro (2015) analysed 66 spots from 36 other grains. Fernandes (2016) analysed 25 spots from 11 grains (Fig. 3).

We add the following sentence:

3

The data from these two studies were obtained in the same conditions as we have worked (see "methods section").

4

Page 10

Figure 8 was modified.

Page 11

The TiO_2 content and its variation is similar to other studied in the region.

We have modified the setence:

5

The TiO2 content and its variation is similar to other columbite-tantalites studied in the region (Neiva and Ramos 2010; Neiva *et al*., 2011).

Page 14

Cassiterite, zircon and struverite inclusions in columbite-tantalite grains indicate a primary magmatic origin. However, the existence of struverite zoned veins may also indicate recrystallization during the subsolidus event, while microlite crystallization appears to be exclusive post-magmatic.

We have rewritten the underlined phrase:

6

The cross-cut character of struverite zoned microveinlets may also indicate crystallization of this Ta-rutile phase during the subsolidus event.