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1 **A multimodal microcharacterization of trace-element zonation and**  
2 **crystallographic orientation in natural cassiterite by combining**  
3 **cathodoluminescence, EBSD, EPMA and contribution of confocal Raman-in-**  
4 **SEM imaging**

5

6 **Running head: multimodal characterization of zonation in cassiterite**

7

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15

16 **ABSTRACT**

17 In cassiterite, tin is associated with metals (titanium, niobium, tantalum, indium,  
18 tungsten, iron, manganese, mercury). Knowledge of mineral chemistry and trace-  
19 element distribution is essential for: the understanding of ore formation, the  
20 exploration phase, the feasibility of ore treatment, and disposal/treatment of tailings  
21 after the exploitation phase. However, the availability of analytical methods make  
22 these characterizations difficult.

23 We present a multi-technical approach to chemical and structural data that includes  
24 scanning electron microscopy (SEM)-based imaging and microanalysis techniques  
25 such as : secondary and backscattered electrons, cathodoluminescence (CL),

26 Electron Probe Microanalyzer (EPMA), Electron Backscattered Diffraction (EBSD)  
27 and confocal Raman-imaging integrated in a SEM (RISE). The presented results  
28 show the complementarity of the used analytical techniques. SEM, CL, EBSD, EPMA  
29 provide information from the interaction of an electron beam with minerals, leading to  
30 atomistic information about their composition, whereas RISE, Raman spectroscopy  
31 and imaging completes the studies with information about molecular vibrations, which  
32 are sensitive to structural modifications of the minerals. The correlation of Raman  
33 bands with the presence/absence of Nb, Ta, Fe (heterovalent substitution), and Ti  
34 (homovalent substitution) is established at a sub-micrometric scale. Combination of  
35 the different techniques makes it possible to establish a direct link between chemical  
36 and crystallographic data of cassiterite.

#### 37 **KEYWORDS**

38 Cassiterite, SEM, cathodoluminescence, EBSD, EPMA, Raman-in-SEM, RISE  
39

#### 40 **SECOND ABSTRACT – LAY DESCRIPTION**

41 Tin is a metal that has been used commercially since the Bronze Age. Cassiterite  
42 ( $\text{SnO}_2$ ), a natural tin oxide, has been the most important source of tin (Sn) since that  
43 time. Sn is also associated with other metals such as titanium (Ti), niobium (Nb),  
44 tantalum (Ta), indium (In), tungsten (W), iron (Fe), manganese (Mn), mercury (Hg) in  
45 cassiterite. A thorough knowledge of its mineral chemistry and trace element  
46 distribution is necessary in the exploration phase for a better understanding of ore  
47 formation, for ore treatment feasibility, and for the disposal of tailings after the  
48 exploitation phase. However, these characterizations remain a challenge due to  
49 numerous analytical insufficiencies.

50 This paper presents a complementary multi-technical approach to chemical and  
51 structural data using a panel of imaging and microanalytical techniques based on  
52 scanning electron microscopy (SEM), chemical imaging, cathodoluminescence in the  
53 SEM (SEM-CL - internal structure, trace element distribution), electron probe micro-  
54 analysis (EPMA – chemical analysis and imaging at the micrometric scale), electron  
55 backscattered diffraction (EBSD – crystallographic mapping) and RISE confocal  
56 Raman-in-SEM imaging (chemical imaging). The correlation of SEM-CL intensity with  
57 crystallographic orientation (EBSD) and trace element distribution (EPMA) can clearly  
58 be established and the influence of each element on luminescence intensity can be  
59 defined at the micrometric scale.

60 In addition, the benefits of using the RISE microscope are highlighted. The analyses  
61 of the same areas of cassiterite grains show the complementarity of the different  
62 analyses and observations performed by SEM-CL imaging, crystallographic  
63 observations (EBSD), elemental analyses and trace elements distribution (EPMA),  
64 and confocal Raman spectroscopy and imaging in the SEM (RISE). The correlation  
65 of  $A_n$  and  $B_{2G}$  Raman bands with the presence/absence of trace elements Nb, Ta, Fe  
66 (heterovalent substitution) and Ti (homovalent substitution) is established at a sub-  
67 micrometric scale. The combination of data collected from the different techniques  
68 makes it possible to link directly both chemical and crystallographic data of  
69 cassiterite.

70

## 71 **INTRODUCTION**

72 Cassiterite ( $\text{SnO}_2$ ) has been and continues to be the most important source of tin  
73 (Sn). Sn is also associated with other metals such as titanium (Ti), niobium (Nb),  
74 tantalum (Ta), indium (In), and tungsten (W), which can complicate ore treatment,

75 although some of these metals can be extracted as by-products. A detailed  
76 knowledge of mineral chemistry and trace element distribution is necessary in the  
77 exploration phase for: a better understanding of ore formation, ore treatment  
78 feasibility, and tailings disposal after the exploitation phase.

79 Cassiterite crystallizes in the tetragonal system with a space group of  $D_{4h}^{14}$ - P 4  
80 /mm. Because of its rutile-type structure, cassiterite can incorporate significant  
81 amounts of Ti, and also trace elements. Similar to rutile, natural cassiterite can  
82 incorporate Fe, Mn, Nb, Ta, In, W, and Hg (Botelho & Moura, 1998; Briskey, 2005;  
83 Cerny et al., 1985; Giuliani, 1987; Izoret et al., 1985; Lerouge et al., 2007; Möller et  
84 al., 1988; Murciego et al., 1997 ; Neiva, 1996 ; Serranti et al., 2002). Characterization  
85 of cassiterite remains a challenge for analytical techniques. EPMA is lacking due to  
86 interference of Sn and trace elements. X-ray emission lines of In  $L\alpha$ , Ta  $M\alpha$  in  
87 wavelength-dispersive X-ray spectroscopy (WDS) can only be solved by the use of  
88 less intense bands (Ta  $M\beta$  or  $L\alpha$  for example). SEM is required due to the  
89 nanometric size of the zonation areas, however, the BSE detector is often not  
90 sensitive enough for the detection of the low content of trace elements.  
91 Cathodoluminescence in the SEM however reveals the trace elements distribution.

92 Raman spectroscopy measures the vibrational frequencies of molecular bonds in a  
93 material. The resulting Raman spectrum is not only unique for a given compound, but  
94 is also sensitive to the local environment. The spectrum reveals structural data; it  
95 provides details on the chemical and structural properties (nature of the functional  
96 groups, symmetry group, lattice defects, etc...) and the crystallinity of mineral  
97 compounds. This method offers a variety of analytical possibilities that include,  
98 among others, identification of different polymorphs (Hope et al., 2001, Gao et al.,  
99 2009), determination of different oxidation states (Das & Hendry, 2011) and

100 crystallographic orientations (Mossbrucker & Grotjohn, 1996), evaluation of  
101 temperature (Lahfid et al., 2010) and stress effects on crystal and molecular structure  
102 (Mossbrucker & Grotjohn, 1997).

103 The availability of Raman spectroscopy in a SEM equipped with imaging detector  
104 (Secondary electrons (SE), backscattered electrons (BSE), cathodoluminescence  
105 (CL), ...), and microcharacterization (EDS, WDS, EBSD) allows morphological,  
106 elemental, chemical, and physical studies without transferring the sample from one  
107 instrument to another. Commercial systems have been available for about 15 years.  
108 These systems use an “on-axis” configuration, i.e. a parabolic mirror is inserted under  
109 the pole piece of the SEM to carry the laser beam to the sample surface and to  
110 collect diffused light for spectroscopic analysis (Wille et al., 2014). The mirror is  
111 connected through a special interface to a conventional  $\mu$ -Raman spectrometer. The  
112 advantage of such a system has been established for different applications, including  
113 forensic applications (Otieno-Alego, 2009) and characterization of individual particles  
114 (Worobiec et al., 2010; Stefaniak et al., 2014), biological samples (Jarvis &  
115 Goodacre, 2004; Jarvis et al., 2004), and mineralogical samples (Stefaniak et al.,  
116 2009; Maubec et al., 2013).

117 Another Raman-in-SEM configuration has been proposed (Van Apeldoorn et al.,  
118 2005) and a commercial version is available, but it is affected by several limitations  
119 (in particular, a limited spectral range). A similar configuration, named “RISE”  
120 (Raman Imaging and Scanning Electron microscopy) has been developed by  
121 manufacturers Tescan (SEM) and Witec (Raman) and major improvements have  
122 been proposed to address the former on-axis configuration (Jiruse et al., 2014). This  
123 new configuration, which can be defined as a “parallel setup,” entails the use of a  
124 precise stage and an image repositioning tool to transfer the sample in the SEM

125 chamber from an SEM position (under the pole piece) to a Raman position (under the  
126 Raman objective). Unlike the “on-axis” setup, the parallel setup makes it possible to  
127 collect Raman spectra without any intensity loss compared to a conventional  $\mu$ -  
128 Raman equipped with the same optical objective. Moreover, Raman mapping is  
129 possible through the collection of a “data cube” (one spectrum collected for each  
130 pixel of the optical image) at high speed (Jiruse et al., 2014).

131 For this study, Cassiterite from the Cadomian Montbelleux Sn  $\pm$ W ore deposit has  
132 been selected because of the millimetric- to centimetric-size and the euhedral forms  
133 of the crystals, its high concentrations of rare metals including Nb, Ta, Fe, Ti, In and  
134 W, and strong chemical zoning compared to cassiterite from Variscan Sn ore  
135 deposits in Brittany, French Massif Central and Galicia (Lerouge et al., 2017). The  
136 substitutions in rare metals were discussed, but their distribution remains unknown at  
137 the crystal scale. This paper presents a complementary multi-technical approach to  
138 chemical and structural data that was tested on cassiterite crystal specimens from  
139 Montbelleux to provide a better characterization of chemical zoning; the approach  
140 includes scanning electron microscopy (SEM), cathodoluminescence in-SEM imaging  
141 (CL), electron probe micro-analysis (EPMA), electron backscattered diffraction  
142 (EBSD).

143 The contribution and features introduced by coupling SEM and Raman spectroscopy  
144 in a coupled SEM-confocal micro-Raman imaging and spectroscopy (RISE) are  
145 highlighted.

146

## 147 **MATERIAL AND METHODS**

### 148 **Materials**

149 Montbelleux is located at Luitré (Ille-et-Vilaine, France) in the Cadomian belt of  
150 northern Brittany, and more precisely in the Mancellian Domain (Ballèvre et al., 2001)

151 (Figure 1). Mineralization occurs as quartz-cassiterite-wolframite stockwork in a  
152 greisen topaz-bearing sodic granite dated at  $490 \pm 15$  Ma by Rb-Sr isochron (Rossi  
153 et al., 1988) and as quartz-wolframite veins in schist at the contact with the batholith  
154 (Chauris et al., 1989). Cassiterite from greisen granite, previously analysed for trace  
155 elements using EPMA, is rich in Fe, Nb, Ta, Ti, compared to other Variscan Sn  
156 deposits in Brittany (Lerouge et al., 2017) (Table 1). Additionally the morphology of  
157 the crystals is of significant interest. Such samples, containing millimetric cassiterite  
158 grains, were selected and prepared as polished sections for mineralogical  
159 investigations (Figure 2).

160

## 161 **Methods**

### 162 Electron beam microscopy and microcharacterization techniques

163 Polished sections were observed in the SEM, under low vacuum conditions  
164 (uncoated samples) for EBSD and RISE and high vacuum conditions (carbon-coated  
165 samples) for CL and EPMA. Elemental mapping and quantitative analyses were  
166 performed using EPMA on carbon-coated polished sections. Carbon-coated polished  
167 sections were coated with 20 nm carbon using a Cressington 308 (Cressington,  
168 Watford, UK).

169 SEM images were obtained using a Tescan Mira 3 XMU (Tescan, Brno, Czech  
170 Republic) equipped with a secondary electron (SE) Everhart-Thornley detector  
171 (Everhart & Thornley, 1960) for high vacuum SE imaging, a low vacuum (LV) SE  
172 detector (Jacka et al., 2003) for LV – SE imaging and a YAG-scintillator  
173 backscattered electron (BSE) detector (Autrata-type BSE detector - Autrata, 1992) at  
174 HV = 25 kV and a panchromatic cathodoluminescence detector (350 – 650 nm)



175 (TESCAN BSE/CL detector). Low vacuum mode (LV) was used, with  $P = 20$  Pa  
176 nitrogen.

177 Orientation maps were obtained using an Edax Pegasus system with a Digiview IV  
178 camera and OIM DC 6.4 software (Edax, Mahwah, USA). Collection was done on  
179 non-coated samples at  $HV = 25$  kV, under low vacuum conditions ( $P=20$  Pa  
180 Nitrogen). Samples had been previously polished using a high quality protocol  
181 including a colloidal silica final step.

182 Wavelength-dispersive X-ray spectroscopy (WDS) elemental mapping was  
183 performed on a Cameca SXFive electron microprobe (Cameca, Gennevilliers,  
184 France) using an accelerating voltage of 20 kV and a beam current of 200 nA.  
185 Complementary spot analyses were performed using an accelerating voltage of 20  
186 kV and intensity of 50 nA to quantify the amount of Nb, Ta, Ti, Fe, and W. Ti  $K\alpha$ , Sn  
187  $L\alpha$ , Nb  $L\alpha$  were measured on PET (pentaerythritol,  $2d = 8.74\text{\AA}$ ), Fe  $K\alpha$ , on LiF  
188 (Lithium fluoride,  $2d = 4.0267\text{\AA}$ ) and Ta  $M\beta$ , W  $L\alpha$  on TAP (thallium acid phtalate,  $2d$   
189  $= 25.75\text{\AA}$ ). Counting time was 10 s for Ti, Fe, and Mn and 40 s for the other  
190 elements. Standards of calibration for EPMA spot quantitative analyses are natural  
191 minerals: cassiterite for Sn, synthetic oxides:  $MnTiO_3$  for Ti and  $Fe_2O_3$  for Fe, and  
192 pure elements: Nb, Ta and W metals. The detection limits of the elements for a single  
193 analysis, given in  $mg.kg^{-1}$ , are for Ti, Fe, Sn, Ta, In and Nb in table 1.

194

#### 195 RISE Raman imaging in the SEM

196 Informations on the local chemistry of zoned cassiterite can be obtained at a  
197 submicrometric scale using Confocal Raman spectroscopy and Imaging. Confocal  
198 Raman imaging was performed on a Tescan-Witec RISE microscope combining a  
199 Tescan Mira SEM integrated with a Witec Confocal Raman Imaging System (Witec,

200 Ulm, Germany). The RISE confocal Raman imaging system is equipped with a  
201 UHTS300 spectrometer, a Zeiss 100x vacuum objective (N.A. 0.75) mounted inside  
202 the SEM chamber, using a 532 nm laser excitation wavelength (Jiruse et al., 2014).

203

## 204 **RESULTS AND DISCUSSION**

### 205 **Zonation and crystal orientation in cassiterite grains using SE, CL, EBSD, and** 206 **EPMA**

207 Cassiterite has been extensively studied with cathodoluminescence (CL) to elucidate  
208 processes of crystal growth (Farmer et al., 1991). CL imaging of a centimetric  
209 cassiterite grain from Montbelleux, acquired in SEM, provides evidence of intense  
210 contrast variations (Figure 2). These contrasts can be attributed to very fine chemical  
211 zoning in trace elements (Hall & Ribbe, 1971; Remond, 1973; Remond et al., 1992)  
212 and to crystal orientations which are known to strongly affect cathodoluminescence in  
213 cassiterite (Hall, 1978).

214 To decrypt the origin of the CL contrast, a small area highlighted with the red arrow in  
215 Figure 2 (figure 3) was analyzed with various techniques. Figure 4 shows the EBSD  
216 inverse pole figure (IPF) map (Figure 4a) the corresponding CL image (Figure 4b)  
217 and the inverse pole figure projection (Figure 4c), acquired from an area of 253x190  
218  $\mu\text{m}^2$ . The EBSD IPF map was collected with a step of 1  $\mu\text{m}$ . A cleaning procedure  
219 (grain dilation) was applied to remove mis-indexed points. The CL and EBSD images  
220 show identical contrasts. Both images show the presence of cracks, the only  
221 topographic features on a polished surface. The change of grey in the SE image  
222 (figure 2) corresponds to an orientation contrast due to electron channelling, a  
223 phenomenon that occurs in a crystal due to the interaction between primary electrons  
224 and the crystal structure (Lloyd, 1987). A similar change is observed also in the

225 EBSD image, providing evidence of mono-oriented grains with twinning. Twinning is  
226 well known in cassiterite as the “elbow twin” (Nespolo & Souvignier, 2015). An  
227 orientation variation of  $68^\circ$  was measured between the twin and the main orientation  
228 of the centimetric grain (Figure 4a), which is close to  $70^\circ$ , the ideal structure (Nespolo  
229 & Souvignier, 2015).

230 The CL image (Figure 4b) shows in addition the presence of alternating dark and  
231 bright bands which are associated with chemical zoning due to the incorporation of  
232 trace elements.

233 A comparison of the three images in Figure 4 reveals that the alternating bands in the  
234 CL image are parallel to the crystal faces and change their orientation in the  
235 corresponding twin crystals.

236 Trace element mapping was conducted by EPMA. EPMA trace element analysis is  
237 challenging due to the existence of interferences between the detectable trace  
238 elements. For example, tantalum (Ta), an element detected in this cassiterite grain,  
239 can be analyzed on the  $M\alpha$  line, which has the highest intensity at  $HV = 15 - 30$  kV.  
240 However, interference occurs between Ta  $M\alpha$  and Sn  $L\alpha^{(2nd\ order)}$  peaks on a TAP  
241 monochromator (Figure 5). The use of the differential mode is a good opportunity to  
242 remove the contribution of this Sn  $L\alpha^{(2nd\ order)}$  peak when the differential mode window  
243 is set to 3 V. A small contribution is still evident (about 1.5 x background level in  
244  $SnO_2$ ). A further reduction of the width of the differential mode window (lower than  
245 800 mV) is not able to completely remove the 2<sup>nd</sup> order contribution. It leads to a  
246 greatly reduced peak intensity, which can be detrimental for trace analysis. As a  
247 result, Ta was collected on Ta  $L\alpha$  at 8.145 KeV. These results are presented in table  
248 2, where only detected elements are reported.

249 Elemental mapping was performed by EPMA (WDS spectrometers) on the same  
250 area than CI and EBSD. Experimental conditions were determined to highlight trace  
251 element distribution. Elemental maps were collected at HV = 20 kV and beam current  
252 = 200 nA, map resolution = 512x512 pixels (stage scanning, step = 1  $\mu$ m). Like CL  
253 image, elemental mapping of trace elements provides evidence of complex chemical  
254 zoning of Nb, Ti, Ta, and Fe. EPMA (WDS) maps (peak intensity) for Ta, Nb, Fe and  
255 Ti are presented in Figure 6 (figure 6 c to f) and compared with SEM-CL and RISE  
256 images obtained from the same sample area. The main zonation domains are  
257 surrounded by white lines to highlight the correspondence between trace element  
258 distribution, CL contrast and Raman spectral variations. According to table 2, Ti is the  
259 most abundant trace element and is regularly distributed in large Ti-rich bands  
260 alternating with fine Ti-poor bands corresponding to crystal growth. Nb and Fe are  
261 less abundant with the same order of content, according to EPMA analyses. On the  
262 contrary, Nb is more heterogeneously distributed throughout the cassiterite crystal  
263 (figure 6d), with irregular domains that are chemically zoned and highly enriched in  
264 Nb, and other crystal domains that are not clearly zoned and are poorer in Nb. The  
265 distribution of these domains compared to the EBSD map (figure 5) also provides  
266 evidence of a line probably corresponding to the limit of the twinning. Ta is present at  
267 very low concentrations (table 2). Comparison of the different elemental maps  
268 indicates that some rare Ta-rich bands seem to correspond to Nb-rich bands, and Ti-  
269 depleted bands to Fe-rich bands.

270 The cathodoluminescence properties of cassiterite depend to a great degree on trace  
271 elements content (Farmer et al., 1991; Hall & Ribbe, 1971; Remond, 1973). The CL  
272 image of the mapped area confirms the relationship between crystal growth and trace  
273 element distribution (figure 6). However, the relationship between trace element

274 distribution and luminescence is complex. The Fe-rich zones seem to correspond to  
275 very low luminescence, and luminescence is quenched when Ti is associated with  
276 Fe.

277 Ti acts as an activator, whereas luminescence is quenched when Fe is present with  
278 Ti. The influence of Ti on the CL activation is shown in various places in this area.  
279 Furthermore, Nb and Ta may turn out to have a negative effect on the panchromatic  
280 cathodoluminescence intensity. However, in numerous places in the observed area,  
281 Ti is associated with Nb and/or (Nb + Ta), elements that act as quenchers of  
282 cathodoluminescence, so that CL intensity prediction is difficult if not impossible. A  
283 general observation is that luminescence in the range of 330-660 nm clearly  
284 decreases with increase of the Nb and Ta concentration.

285

#### 286 **Contribution of RISE Confocal Raman imaging integrated in a SEM**

287 Raman spectroscopy provides qualitative information on the presence and  
288 distribution of trace elements in cassiterite, based on the presence, intensity, and  
289 position of Raman bands. The characteristic Raman bands for SnO<sub>2</sub> are the A<sub>1G</sub>  
290 band at 638 rel. 1/cm and B<sub>1G</sub> band at 741 rel. 1/cm (figure 7b). They correspond to  
291 the symmetric and asymmetric stretching of the Sn-O bonds respectively. Upon  
292 incorporation of different elements in the crystal lattice, shifts, broadenings and the  
293 appearance of additional Raman bands in the Raman spectrum will occur. According  
294 to Wang and co-authors (Wang et al., 1993), a variation of several peaks in Raman  
295 shift intensity is observed for the trace element ratio (Nb + Ta)/(Fe + Mn).

296 The primary problem for Raman analysis on such a cassiterite grain is related to the  
297 location of the region of interest, which cannot be analyzed - or at least not easily - by  
298 optical microscopy. As a result, SEM SE (secondary electrons), BSE (backscattered

299 electrons), and CL imaging were used to determine the precise location of the area of  
300 interest (mainly based on the co-location of cracks in the selected area). After  
301 locating the region of interest, the sample was transferred inside the vacuum  
302 chamber to the confocal Raman measuring position for further analysis. A Raman  
303 image ( $200 \times 200 \mu\text{m}^2$ ) was collected from the region of interest, by acquiring a 2D  
304 array of  $200 \times 200$  complete Raman spectra with an integration time of 0.08s per  
305 spectrum. The total acquisition time for the Raman image consisting of 40000 spectra  
306 was 53 minutes. The 2D array of Raman spectra was analyzed with multivariate  
307 spectral analysis methods such as Cluster Analysis, described in details by T. Dieing  
308 and W. Ibach (Dieng & Ibach, 2010) The Raman spectra obtained from these  
309 analysis are presented in Figure 7a. All four spectra contain the main  $A_{1G}$  band at  
310  $638 \text{ rel.1/cm}$  indicating the presence of  $\text{SnO}_2$  in the analyzed crystal. The distribution  
311 of the four components in the analyzed sample area is presented in the color coded  
312 Raman image (Figure 7a). The colors in the Raman image match the colors of the  
313 Raman spectra. As shown previously, based on EBSD and EPMA analyses, this part  
314 of the grain is characterized by different areas including main/twin crystal orientation  
315 and high/low trace element concentrations. The overlay of the Raman image with the  
316 CL image (Figure 7a) highlights the sensitivity of Raman spectroscopy to grain  
317 orientation and incorporation of trace elements in the crystal structure of  $\text{SnO}_2$ .

318 Beside the  $\text{SnO}_2$  characteristic Raman bands, the spectrum in Figure 7b (spectrum  
319 d) contains a Raman band at  $840 \text{ rel. 1/cm}$  which can be associated to the  $A_n$   
320 vibrational mode of Nb (Wang et al., 1993). By comparing the Raman image (Figure  
321 7a) with the elemental distribution of Nb (Figure 6b), a clear correlation can be made.  
322 On the other hand, the  $A_n$  band is weak or not visible on the green and purple spectra  
323 (figure 7b spectra a and c), those corresponding to a low Nb content. Low Nb

324 coupled with a low Ti concentration is observed for the purple area (figure 7a and  
325 figure 7b spectrum a), and low Nb coupled with a high Ti concentration is noted for  
326 the green area (figure 7a and figure 7b spectrum c). The  $B_{2g}$  band at  $741\text{ cm}^{-1}$  is  
327 strong on the purple spectrum (figure 7b spectrum a) and quite weak on the green  
328 one (figure 7b spectrum c). The intensity of this band is high compared to the  $A_g$   
329 band when characterized by a medium to high Nb content associated with Ta ( $\pm$  Fe)  
330 and a low Ti content (purple and blue spectra - figure 7b spectra a and d). In the  
331 opposite case, the intensity of the  $B_{2g}$  band is low compared to the  $A_g$  band when Nb  
332 and Ta contents are low and Ti is high (green spectrum - figure 7b spectrum c).  
333 According to Izoret et al (Izoret et al., 1985), the substitution Sn – Ti in cassiterite is  
334 isomorphic and homovalent ( $\text{Sn}^{4+} / \text{Ti}^{4+}$ ) whereas at the other end, the Sn – (Nb,Ta)  
335 substitution is heterovalent ( $\text{Sn}^{4+} / \text{Nb}^{5+}, \text{Ta}^{5+}$ ) with the necessity of local charge  
336 compensation (for example with  $\text{Fe}^{3+}$ ).  
337 In addition, according to EPMA map of tungsten W (data not shown), the blue  
338 spectrum (figure 7b spectrum b) could be attributed to wolframite.  
339 Thus a relationship can be established between these Raman spectral differences  
340 and trace element contents, which agree with the conclusions of Wang and co-  
341 authors (Wang et al., 1993). RISE imaging enables a direct link of Raman spectra to  
342 trace element distribution and crystal orientation at the micrometric / sub-micrometric  
343 scale in  $\text{SnO}_2$  minerals.

344

## 345 **CONCLUSION**

346 In this study, cassiterite zonation and orientation was explored using a panel of SEM-  
347 based imaging and microanalysis techniques. The panchromatic intensity of  
348 cathodoluminescence of a cassiterite grain is affected by both crystal orientation and

349 trace element distribution. The correlation of CL intensity with crystallographic  
350 orientation (EBSD) and trace element distribution (EPMA) can be clearly identified  
351 and the influence of each element can be defined at the micrometric scale. The  
352 influence of trace elements on luminescence intensity is clearly established.

353 In addition, we present the benefits of using confocal Raman imaging integrated in a  
354 SEM (RISE microscopy). Cassiterite grain analyses on the same area show the  
355 complementarity between the various analyses and observations performed by SEM-  
356 CL imaging, crystallographic observations (EBSD), elemental analyses and trace  
357 element distribution (EPMA), and confocal Raman spectroscopy / imaging. The  
358 advantage of using RISE imaging and spectroscopy at a sub-micrometric scale has  
359 been highlighted because of its ability to detect, discriminate, and characterize sub-  
360 micrometric areas and phases present in a complex cassiterite grain (down to less  
361 than 400nm according to Jiruse et al., 2014), in correlation with trace elements and  
362 crystallographic orientation. The presence of Ta and Nb (heterovalent substitution)  
363 correlates with increased  $A_n$  (~ 840 1/cm) and  $B_{2g}$  (~ 741 1/cm) band intensities,  
364 whereas the Raman spectrum of an area with a low Nb and Ta coupled with a high Ti  
365 content (homovalent substitution) appears to exhibit low intensity  $A_n$  and  $B_{2g}$  bands.  
366 The combination of data collected from the different techniques makes it possible to  
367 link directly both chemical and crystallographic data and the changes in the Raman  
368 spectrum of cassiterite.

369



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499

500 Tables

501 Table 1: Average contents of main trace elements in cassiterite from Montbelleux by  
502 EPMA (after Lerouge et al. 2007).

503 Table 2: Average contents of main trace elements in the different area identified by  
504 RISE microscopy (from EPMA analysis). Detection limit for each element is given in  
505 brackets

506

507 Figures

508 Figure 1: Location of Montbelleux deposit and SEM (BSE) images of the cassiterite  
509 surrounding minerals (after Lerouge et al. 2017).

510 Figure 2: SEM – panchromatic cathodoluminescence image of a centimetric  
511 cassiterite grain (red arrow: position of analyzed area – see figure 3)

512 Figure 3: Secondary electrons (a) and panchromatic cathodoluminescence (b)  
513 images of the Cassiterite grain area

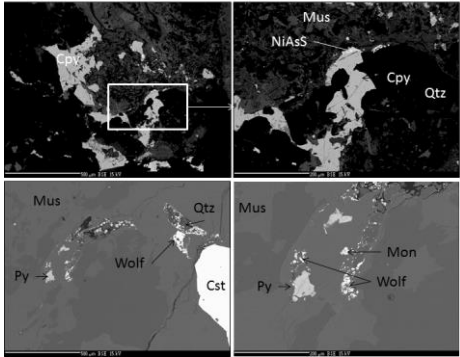
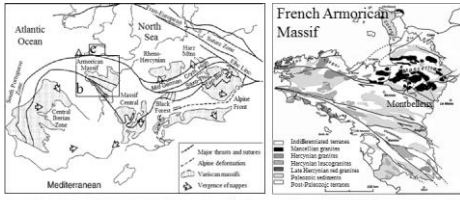
514 Figure 4: EBSD orientation map of the area of interest (a), CL image (b), and [001]  
515 inverse pole figure (c)

516 Figure 5: WDS interference Ta  $M\alpha$  / Sn  $L\alpha$  (2nd order) on a TAP monochromator

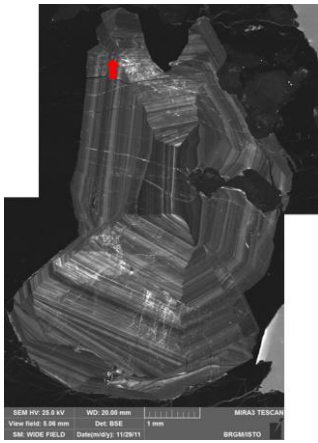
517 Figure 6: comparison of cathodoluminescence image (CL) (a) and RISE imaging map  
518 (b) with elemental mapping for trace elements Ta (c), Nb (d), Fe (e) and Ti (f) –.

519 Fissures are indicated in red. White lines give limits of small domains presenting  
520 different orientations of growth and low luminescence.

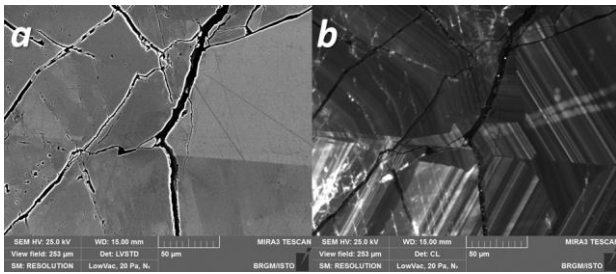
521 Figure 7: Raman map superimposed on CL image (a) and Raman spectrum of each  
522 area identified on the Raman map (b) - average content of trace elements in areas  
523 identified by Raman imaging (c - see Table 2) expressed in atom per formula unit  
524 (a.p.f.u) for the understanding of the substitution in the mineral.



525



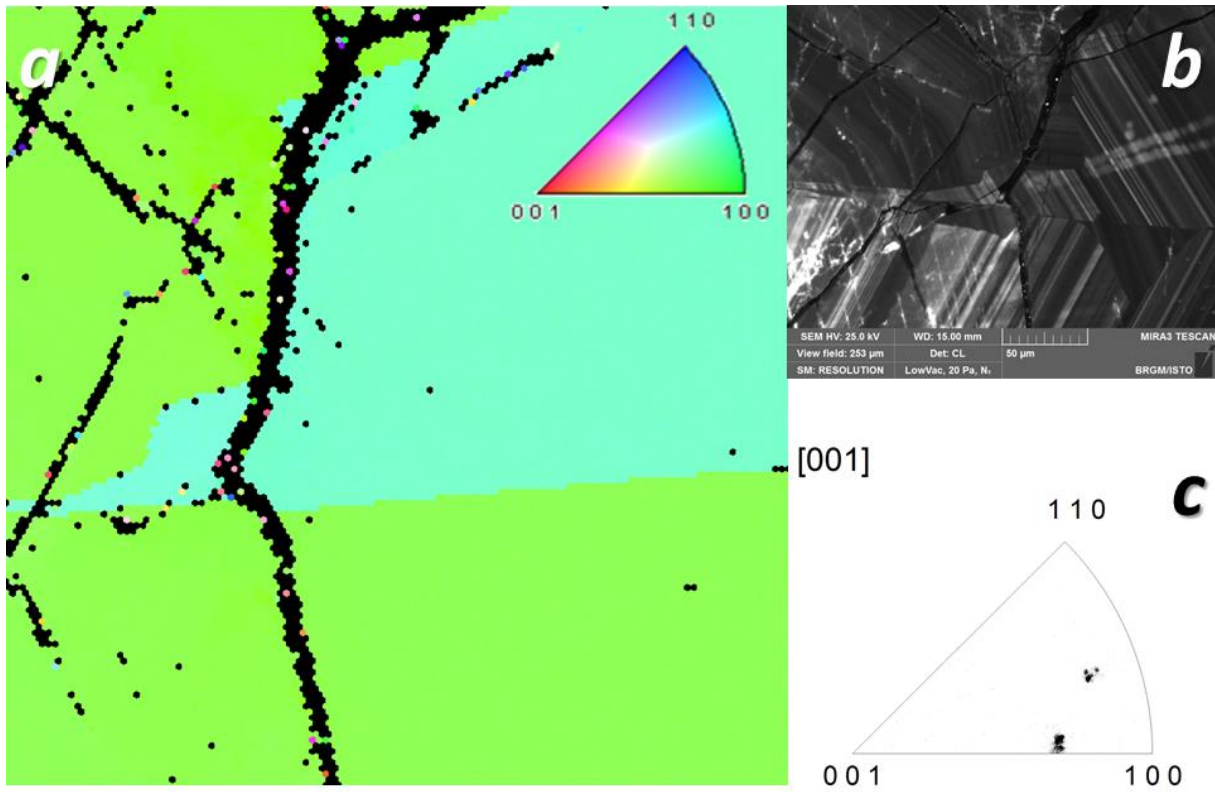
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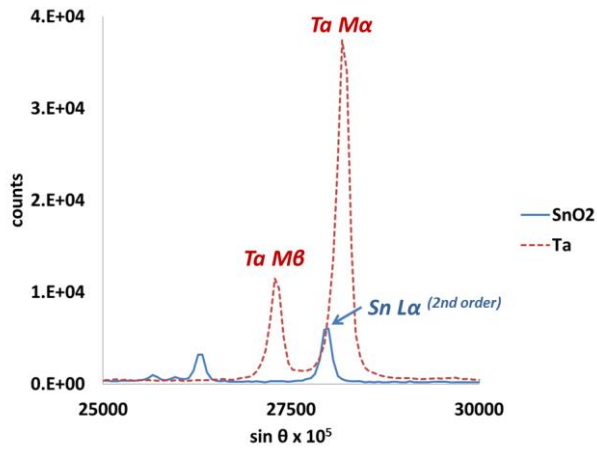
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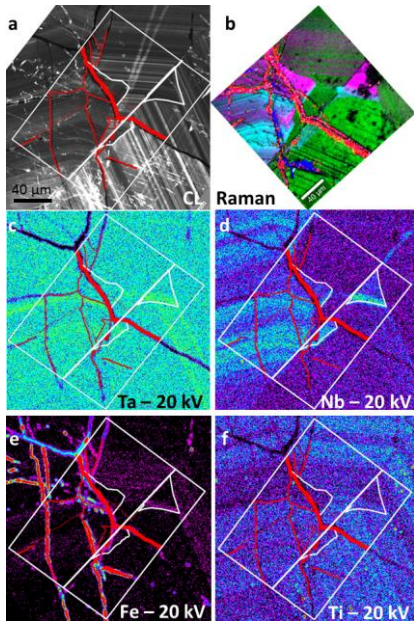




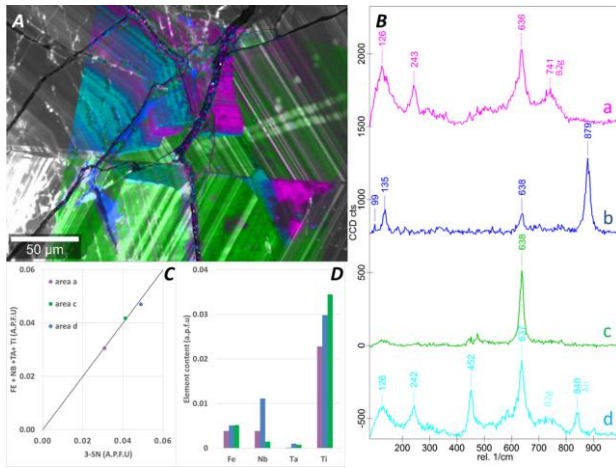
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532

533 Table 1: Average contents of main trace elements in cassiterite from Montbelleux by  
 534 EPMA (after Lerouge et al. 2007).

535

number of analyses	SnO <sub>2</sub> wt %	Trace element contents (mg.kg <sup>-1</sup> )					
		Fe	In	Nb	Ta	Ti	
45	average	98.97	2568	519	3901	5809	2635
	std.	0.74					
	dev.		1402	204	3487	4325	1377

536

537 Sn 2.92±0.04 Fe 0.02±0.01 Nb 0.02±0.02 Ta 0.01±0.01 Ti 0.02±0.01 O<sub>2</sub>

538

539 Table 2: Average contents of main trace elements in the different area identified by  
540 RISE microscopy (from EPMA analyses). Detection limit (in %) for each element is  
541 given in brackets

542

<b>Area</b>	<b>TiO<sub>2</sub></b> <i>(0.03)</i>	<b>FeO</b> <i>(0.035)</i>	<b>Nb<sub>2</sub>O<sub>5</sub></b> <i>(0.018)</i>	<b>SnO<sub>2</sub></b> <i>(0.163)</i>	<b>Ta<sub>2</sub>O<sub>5</sub></b> <i>(0.050)</i>
<b>a</b>	0.405	0.061	0.114	99.413	0.000
<b>c</b>	0.612	0.083	0.043	99.223	0.000
<b>d</b>	0.531	0.082	0.329	99.009	0.050

543

544