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**High pressure and temperatures during the early stages of tungsten deposition at
Panasqueira revealed by fluid inclusions in topaz**

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25

26 **Abstract**

27

28 The Variscan vein-type Panasqueira W-Sn(Cu) deposit, one of the main tungsten deposits in
29 Western Europe, has a long and complicated geological history. The first vein infillings, which
30 consist of the quartz-wolframite association as well as the first generation of topaz, underwent
31 significant deformation. As a consequence, most fluid inclusions of the earliest hydrothermal
32 event are deformed and destroyed. Two preserved fluid inclusion assemblages are, however,
33 found in the topaz overgrowth band and are dense aqueous-carbonic inclusions as well as
34 dense CO₂ dominated fluid inclusions. The P-T conditions of fluid trapping are constrained by
35 using the intersection between isochores, as well as graphite-water equilibrium data and yield
36 the following trapping conditions: 500 ± 20°C and 250 ± 20 MPa. These P-T conditions are
37 incompatible with fluid unmixing. Fluid chemistry results from water-graphite equilibrium,
38 probably in metapelites, at two distinct temperatures: around 450-500°C for the predominant
39 aqueous-carbonic fluid, and higher temperatures of maximal 550°C for the CO₂-rich fluid
40 enriched in N₂. These P-T estimates are consistent with deep crustal levels around 8-10 km
41 depth and a high geothermal gradient around c. 60°C/km⁻¹. The ascending non-magmatic
42 fluids, enriched in volatiles, are essential in the ore genesis.

43 The high thermal gradients may be related either to new magma pulse after the formation of
44 the Panasqueira granite intrusion or to anomalous heat flux produced by the hot fluids
45 ascending from migmatitic levels present at greater depth. This hypothesis necessitates to
46 consider the role of a crustal weakness, which is attested both by the successive intrusions of
47 several granitic magmas at the same place, and the presence of inherited quartz filled
48 structures so-called Seixo-Bravo found only in the Panasqueira area.

49

50 **Keywords:** Metamorphic fluids; Topaz; Tungsten; P-T path; Deep crustal level; Panasqueira.

51

52

53 **1. Introduction**

54

55 The Variscan Panasqueira W-Cu-Sn deposit, one of the prominent W deposits in Western
56 Europe, has for a long time been considered a granite-related stockwork of quartz-wolframite
57 veins, related to a concealed intrusion, at a rather shallow crustal level (Kelly and Rye, 1979).
58 The paragenetic succession established in this early pioneering study was later corrected and
59 completed by Polya et al. (2000), Lourenço (2002), and Pinto et al. (2015). It was the basis of
60 the paragenetic scheme used by all further studies.

61 On this basis, several fluid inclusions (FI) studies intended to estimate ore depositing
62 conditions (Kelly and Rye 1979, Bussink 1984, Noronha et al. 1992, Polya et al. 2000,
63 Lourenço 2002, Lecumberri-Sanchez et al. 2017, Jaques and Pascal 2017). Earliest studies
64 by Kelly and Rye (1979) focused primarily on quartz and, to a lesser degree, on apatite and
65 siderite. They used a debatable postulate that fluids were trapped under conditions close to
66 boiling, and homogenisation temperatures have therefore been considered as trapping
67 temperatures. Kelly and Rye (1979) concluded, therefore, that most mineral assemblages in
68 the deposit formed at around 230-360°C at low pressures (below 15 MPa), the concealed
69 granite intrusion controlling a unique hydrothermal megacycle. They concluded that the burial
70 was rather shallow, between 600 m and 1300 m at a maximum. Bussink (1984) adopted the
71 same line of interpretation, e.g., the fact that the presence of both vapour-dominated inclusions
72 and aqueous carbonic liquids, is indicative of volatile unmixing. He considered the ore
73 deposition depth to be between 1600 and 2000 m with pressure around 15 MPa, with veins
74 connected to the surface. However, this hypothesis could not explain the presence of some
75 dense fluid inclusions, leading Bussink et al. (1984) to suggest a significant overpressure (150
76 MPa) at the very first stage of vein opening. Then, Polya (1989) analysed FI leachates after
77 crushing and indicate that ore-forming fluids were low salinity aqueous fluids of meteoric origin,
78 in equilibrium with K-feldspar, albite and muscovite at 350-400°C. The inferred pressure, less
79 than 500 bars, was deduced from the available literature. Later, Noronha et al. (1992)
80 proposed that fluid pressure was fluctuating below lithostatic pressure. They did not provide,
81 however, precise ranges of temperatures and pressures, except that temperatures could be
82 higher than 350°C. Foxford et al. (2000) considered the vein swarm as formed through
83 extensional failure driven by hydraulic-valving at moderate differential stresses in a
84 compressive crustal regime. Based on statistical data on the geometric characteristics of the
85 veins and deformation models, they deduce that the veins developed in the supralithostatic
86 pore pressure region beneath a low permeability cover. Still, they did not venture to provide a
87 pressure estimate in a pressure-depth diagram.

88 Lourenço (2002) confirmed that mineralisation was associated with CO₂-CH₄-N₂ aqueous-
89 carbonic fluids with low salinity (5 – 10 wt% NaCl equiv.) and minimum entrapment
90 temperature close or below 300°C. As Noronha et al. (1992), Lourenço (2002) concluded that
91 most fluids are of metamorphic derivation. Campbell et al. (1988) and Lüders (1996) studied
92 using infra-red microscopy wolframite-hosted fluid inclusions. In wolframite from an unknown
93 stage, Lüders (1996) described most FI as aqueous fluids with salinities ranging from 7 to 20
94 wt% NaCl equiv., as CO₂ could not be detected by microthermometry. On the contrary,
95 Campbell et al. (1988) considered the predominant FIs in wolframite to be rich in volatiles, but
96 microthermometric measurements could not confirm CO₂. However, they found two three-
97 phase FIs containing liquid CO₂ but did not provide data on this type of FI. Using LA-ICP-MS

98 analyses of unspecified volatile-bearing FI from the quartz veins, Lecumberri-Sanchez et al.
99 (2017) concluded that fluids were magmatic and transported W, the wolframite precipitation
100 being entirely dependent on iron availability in the altered wall rocks.

101 Isochores in detailed P-T diagrams lack in most studies, except that of Jaques and Pascal
102 (2017). The latter proposed a rather high-pressure estimate (c. 300 MPa) using a temperature
103 issued from arsenopyrite geothermometry. Other independent temperature estimates were
104 recently acquired by Codeço et al. (2017), using the Ti-in-quartz geothermometer, and Codeço
105 et al. (2019) using B isotopes. The Ti-in-quartz geothermometer, applied to wall rock
106 hydrothermal quartz from the earliest stage of tourmalinisation preceding the W deposit, yields
107 estimates of 420–550 °C, for an inferred pressure of 100 MPa derived from Foxford et al.
108 (2000), and 404–530°C, for a lower value of 20 MPa, closer to that of Kelly and Rye (1979).
109 The B thermometer proposed by Codeço et al. (2019) assumes isotopic equilibrium between
110 tourmaline and muscovite, and yielded a range of temperatures, from a 400-460°C average
111 interval for the formation of the vein selvages down to c. 250°C for the latest stages. These
112 estimates are in sharp contrast with most of the previously published data. Finally, other
113 studies such as Launay et al. (2018) focused on fluid flow vectors deduced from tourmaline
114 growth features at the vein margins and showed that fluids flowed radially around the
115 greisenised cupola; hence they equally concluded for a magmatic origin for the fluid.

116 In brief, although extensively studied, the P-T-X evolution of ore fluids at Panasqueira during
117 its long history remains controversial, as most published estimations disagree with each other.
118 Furthermore, preliminary FI studies of the first generation of quartz (QtzI) have shown that
119 decrepitation and deformation destroyed most early fluid inclusions trapped in quartz
120 (Cathelineau et al., 2017). This critical fact, unfortunately, was overlooked in all previous
121 studies. The lack of consensus on the P and T evolution at Panasqueira prompted us to
122 perform a detailed review of fluid inclusion assemblages. Recent mine galleries at Panasqueira
123 have provided new and excellent samples, in particular for the early-stage mineral
124 assemblages, such as topaz veins. These veins crosscut the oxide (wolframite-quartz) stage
125 assemblages, and show exceptionally well-preserved fluid inclusions. We studied thus early
126 mineral stages (wolframite-quartz, and then topaz-pyrrhotite) in detail by using all available
127 tools necessary for the determination of detailed bulk chemistry and fluid density to propose
128 an accurate P-T reconstruction and discuss the depth and factors controlling the ore genesis.

129

130

131 **2. Geology and sampling**

132

133 The Panasqueira W–Sn–Cu deposit is located in the Portuguese part of the Variscan Central
134 Iberian Zone (CIZ) (Fig. 1A and B). The mine, active for more than 100 years, was for a long

135 time one of the largest tungsten producers in Western Europe. The sum of the past production
136 of at least 88 kt W in 1947–2014 (Vigne et al., 2018) and of remaining reserves + resources of
137 ~ 23 kt W (Almonty Industries et al., 2016), yield to at least c. 111 kt W, thus contributing for
138 more than one third to the CIZ tungsten endowment.

139 The deposit occurs in greenschist facies micaschists belonging to the Beira Schists Complex
140 (Diez-Fernandez et al., 2013), which forms part of the main autochthonous terrane in the
141 Central Iberian Zone. This terrane comprises a thick sequence of late Ediacarian-Cambrian
142 metasedimentary rocks, the Schist-Greywacke Complex, also called Beira Group, overlain
143 unconformably by the Early Ordovician Armorican Quartzite as shown in the cross-section in
144 Figure 1C (Diez-Fernandez et al., 2013). The metasedimentary package is divided into three
145 units (Diez-Fernandez et al., 2013): (1) a lower unit (≥ 2000 m thick), monotonous alternation
146 of slates and sandstones (Ediacarian), with at the top intercalation of thick (up to 400 m)
147 carbonate levels and several black slate layers (encompassing the upper Ediacarian and lower
148 Cambrian); (2) a middle unit (~500 m thick), characterised by abundant sandstones and
149 conglomerates; and (3) an upper unit (~1000 m thick), mostly composed of greenish-grey
150 slates, with sandstone and conglomerate layers.

151 The tectonic and thermal Variscan history of the CIZ, which begins in the Early Carboniferous
152 and ends in the Early Permian, is subdivided into five deformation events, D1 (350 ± 4 Ma) to
153 D5 (290 Ma) (Diez-Fernandez et al., 2016, Diez-Fernandez and Pereira, 2017, Rubio-Pascual
154 et al., 2013). The D2 -D5 evolution is characterised by large-scale crustal melting, resulting
155 from a combination of mid-crustal post-thickening heating and mantle-derived heat input at the
156 base of the continental crust (Pereira et al., 2017). The D3 to D5 evolution corresponds to a
157 long series of episodic intra-crustal transcurrent deformation, initiated at ca. 315-310 Ma by
158 the development of 1 km- to 10 km-sized NW-SE to N-S upright F3 folds, with an S3 axial-
159 plane schistosity, and followed by D4 (c. 309-305 Ma) left-lateral and D5 (c. 304-295 Ma)
160 dextral faulting (Diez-Fernandez et al., 2017; and references therein). Crustal melting and
161 concomitant mantle-derived heat input were continued throughout D3 to D5, with the pervasive
162 emplacement of syn- to post-kinematic granite plutons, in three pulses roughly coincident with
163 the D3 to D5 events: syn-kinematic porphyritic biotite monzogranites and leucogranites (c.
164 315-310 Ma); late-kinematic D3 (c. 309-301 Ma) and post-kinematic (c. 295-287 Ma) biotite \pm
165 cordierite monzogranites and granodiorites, with ferroan-potassic sub-alkaline granites at c.
166 295-290 Ma (e.g., Dias et al., 1998; Mateus and Noronha, 2010; Sant'Ovaia et al., 2010;
167 Fernandez-Suarez et al., 2011). Water-absent dehydration melting (biotite incongruent
168 melting) produced cordierite-bearing diatexites in the cores of D2 migmatitic domes (Pereira-
169 Gomez and Rodriguez-Alonso, 2000).

170 The Panasqueira deposit consists of a swarm of sub-horizontal mineralised quartz veins also
171 containing Sn and Cu and extending for over 10 km² with a vertical extent of around 300 m

172 (Fig. 2). The formation and opening of the veins have been variously interpreted in terms of
173 either extension during granite emplacement (Foxford et al., 2000) or to transpression with
174 joint development during the late orogenic stages (Jacques et al., 2017). Sets of barren quartz
175 veins, the so-called “Seixo Bravo” veins, are crosscut by the sub-horizontal W-quartz veins.
176 They are decimetric to metric in thickness and extension between 100 to 200m. They are
177 densely distributed in the mine area but are quasi-absent outside the deposit. They are sub-
178 vertical, forming conjugate sets at c. N110-120° and 150-170°E of quartz filled veins. They are
179 highly deformed, the veins having suffered buckling and mullioning during S3, and are
180 therefore clearly late kinematic for D3. A large, concealed granite body with a laccolith shape
181 (Ribeiro, 2017) is associated with a contact metamorphic aureole outcropping as spotted
182 schists. At the top of this body, layered magmatic and a cupola of rare metal granites (Kelly
183 and Rye, 1979, Bussink, 1984, Marignac et al., 2020) are more or less affected by
184 greisenisation and crosscut by the mineralised vein system.
185 Samples studied come from two main zones (Fig. 2): i) the topaz zone located in the south-
186 western part of the deposit (mining works at level 1, in particular, the adit L1-D29-513-AW14,
187 eastern side), and ii) wolframite-quartz veins from the “bank area” located at the first level, now
188 inaccessible, but for which an extensive sampling from years ‘70s was available by the authors,
189 and from level 3.

190

191 **3. Methods**

192 *3.1. Paragenetic associations*

193 Following petrographic examination with an OLYMPUS BX51 (transmitted and reflected light)
194 optical microscope and a VHX-200 KEYENCE digital microscope, selected samples were
195 studied with a Schottky-FEG (Field Emission Gun) JEOL J7600F scanning electron
196 microscope (SEM) equipped with an SDD-type EDS spectrometer at the GeoRessources
197 Laboratory (Nancy, France). Backscattered electron (BSE) images were obtained by setting
198 the acceleration voltage at 15 kV.

199 Micro-XRF mapping was carried out using the Bruker-Nano M4 Tornado instrument. This
200 system has an Rh X-ray tube with a Be side window and polycapillary optics giving an X-ray
201 beam with a diameter of 25-30 µm on the sample. The X-ray tube was operated at 50 kV and
202 200 µA. X-rays are detected by a 30 mm² xflash® SDD with an energy resolution of <135 eV
203 at 250,000 cps. All analyses were carried out at 2 kPa vacuum. Main elements such as U, Ca,
204 Mg, Mn, Fe, Ti, Al, K, Na, and Si were mapped, and composite images were generated.

205

206 *3.2. Fluid inclusions*

207 Fluid evolution has been studied by looking at relationships between fluid inclusions, their host
208 mineral, the geometry of the host microstructures, and the location of ore minerals. Fluid

209 inclusions assemblages were related to the relative chronology of mineral assemblages.
210 Notation of the fluid inclusion types follows nomenclature previously published (Boiron et al.,
211 1992), which takes into account the nature of the dominant chemical phases and phase
212 changes observed. It is based on the total homogenisation Th (L–V to the vapour noted V, L–
213 V to the liquid noted L) and the quantity of C–H–O–(N–S) species: subscript c, when C–H–O–
214 S species are the only components and water is not visible; c-w, when water and
215 homogenisation of carbonic phase are observable; w-c, when both water and volatiles (CO₂,
216 CH₄, and N₂ species) are present, but gases are detected only by clathrate melting and Raman
217 spectroscopy.

218 Microthermometry was carried out on fluid inclusions using a Linkam® MDS600 heating-
219 cooling stage, adapted to an Olympus® microscope at the GeoRessources laboratory in Nancy
220 (France). The following microthermometric parameters have been measured: the melting
221 temperatures of ice (T_m ice), CO₂ melting and clathrate dissociation (T_m CO₂ and T_m cl), CO₂
222 homogenisation (Th CO₂), and total homogenisation temperature (Th). The temperatures of
223 phase changes have a precision of about ±0.1 °C for T_m ice, T_m CO₂, Th CO₂, and T_m cl, and
224 ±1 °C for Th, whereas the accuracy, is better than 0.5°C in the low-temperature range and
225 better than 5°C at high temperatures. The volumetric fraction of the volatile phase (fvp) was
226 estimated by reference to the volumetric chart of Roedder (1979).

227 The analysis of gas species of the volatile phase was performed with a Dilor-Labram Raman
228 microspectrometer at GeoRessources in Nancy (France) on aqueous-carbonic inclusions
229 previously studied by microthermometry (Dubessy et al., 1989). The density of the volatile
230 phase (dv) and the bulk composition were calculated using programs (Q2 and ICE) developed
231 by Bakker (1997) using equations of state from Thiery et al. (1994) and Duan et al. (1996).
232 Isochores of fluid inclusions have been calculated using the ISOC program (Bakker, 2003)
233 based on the equations of state from Bowers and Helgeson (1983) reviewed by Bakker (1999).

234

235 **4. Results**

236 **4.1 Mineral associations: wolframite-quartz and topaz-sulphide**

237

238 The detailed paragenetic succession of the first mineral infillings, which is the prerequisite to
239 any reliable geochemical or fluid inclusion study, is presented in Fig. 3. The following
240 observations concern, thus, the three early paragenetic stages corresponding to the early
241 tourmaline (+rutile) stage, which precedes the oxide stage (quartz-wolframite), responsible for
242 more than 90% of the exploited wolframite, and the sulphide stage (pyrrhotite, sphalerite,
243 chalcopyrite). These stages broadly correspond to those already defined by Kelly and Rye
244 (1979) and used in all further studies. The differences concern a series of minerals which are
245 found spatially associated with these three first assemblages but considered as formed later

246 on by dissolution and replacement (muscovite, apatite, siderite). Thus, geodes formed during
247 a later stage so-called IV, are found sporadically in the deposit and consist in nice euhedral
248 infillings of quartz IV, and other minerals noted IV by reference to stage IV: wolframite IV, (rare
249 topaz IV), abundant arsenopyrite, muscovite, cassiterite IV, apatite and siderite. Besides, in
250 addition of cassiterite IV, other later cassiterites were also found during later stages (Pinto et
251 al.,2015).

252 In the present work, we only considered non-debatable textural features for establishing the
253 relative vein chronology for the main and earliest stages, and do not discuss the accessory
254 minerals found in fissures, reopened selvages, vugs, and dissolution zones. Only two criteria
255 were used: (i) the intersection of veins (or veinlets or microcracks), each bearing a distinct
256 mineral assemblage (notably, a monomineralic one, fortunately frequently encountered), and
257 (ii) the infilling sequence in a demonstrably open space. Ideally, these two criteria are
258 simultaneously used, for instance, in the crack-seal veins. These criteria have been applied to
259 each scale of observation, from the “outcrop” level (mining works) to the microscopic level. At
260 the sample scale, the required scale of observation may be often wider than the thin section
261 dimensions, a difficulty related to the endowment of the deposit, but which can be alleviated
262 by using sample-scale scanning systems (micro-XRF).

263 At the “pillar” scale, a “pulsed” story is evident, marked by the succession of a series of
264 opening/closing events, each one with its own mineralogical and structural imprint, defining a
265 series of three early stages (I to III) (Fig. 3). Each of the first three stages (I-III) represents a
266 full cycle of opening-complete infilling by a specific set of minerals:

267 - Stage I: after pervasive tourmalinisation of the wall rocks (Stage 0), wolframite (Wfm)
268 crystallised as euhedral prisms at the fracture edges (Carocci et al., 2018, 2019, 2020). It was
269 followed by massive quartz (Qtz I) precipitation following alpine fissure type opening, with
270 development of euhedral Wfm and then a nearly full vein infilling by Qtz I (Fig. 4a to d).

271 - Stage II: a renewal of opening and vein filling by quartz and wolframite succeeded to stage I.
272 Comb quartz precipitation occurred in a marked crack-seal mechanism. Meanwhile,
273 deformation with a multi-crack opening sub-parallel to the vein plane happened in the stage I
274 veins. As a result, wolframite crystals were fragmented (Fig. 4e and 4f), and each crack was
275 healed/sealed by thin, newly formed quartz Qtz II. Together, these two stages were
276 responsible for more than 90% of the vein infilling at Panasqueira, and contain most of the W
277 deposited. Thus, photographs and the scheme Fig. 4 (b, c, d, and e) are representative of
278 hundreds of veins identified in the deposit. Wolframite is, however, heterogeneously
279 distributed, and is often absent on the edge of veins.

280 - Stage III: sulphides filled large volumes developed around fracture zones affecting the
281 previous veins from Stage I-II. The openings are generally oblique to the oldest Wfm-Qtz I or
282 Qtz II elongation.

283 Three substages are distinguished: III-a, characterised by topaz deposition, with subordinated
284 cassiterite; III-b, marked by the sulphide deposition (sphalerite, pyrrhotite, chalcopyrite, in this
285 order, pyrrhotite being by far the most abundant); and III-c, corresponding to the replacement
286 of pyrrhotite by pyrite (Fig. 3). Owing to the utmost importance of topaz for deciphering the P-
287 T-X fluid evolution (see below), some details are now provided on sub-stage III-a.

288 Topaz is commonly found as veins, subparallel to the earlier quartz veins. Compared to stage
289 I-II quartz veins, the topaz veins either developed independently or intersected them. Topaz
290 veins are either independent veins out of the stage I-II quartz veins or crosscut them. Separate
291 topaz veins typically present the following sequence: first comb topaz; sulphides, first
292 sphalerite, then pyrrhotite (Fig. 5 a and b). Thus, the topaz deposition immediately preceded
293 sulphide deposition. The recent expansion of mine works towards the SW revealed a specific
294 abundance of these topaz-sulphide veins; this area is therefore called the “Topaz zone” in
295 which cassiterite is widespread (Fig. 2). This local abundance is also pointed out by Mateus et
296 al., (2020) who confirm that these veins are devoided of muscovite selvage, and extend from
297 the SW to the NW sector of the mine. Similar topaz veins or veinlets crosscut the QtzI-W-ore
298 veins (Fig. 5 c and d) and precede later massive sulphides from stage III-b (Fig. 5b). Topaz
299 also replaces quartz as disseminated crystals, associated with cassiterite, and locally related
300 to ductile shearing of Qtz I or Qtz II (Fig. 6). Finally, topaz crystallised in between host rock
301 and wolframite, at the vein selvage, thanks to the reopening of this boundary. This latter
302 observation explains why topaz was considered part of stage I by Kelly and Rye (1979) and
303 subsequent workers. It is nevertheless repeatedly observed that topaz overprinted wolframite.
304 The wolframite clasts are thus included in topaz, as demonstrated by the micro XRF mapping
305 (Fig. 7).

306 Thus, topaz formed during a single episode, after stage I wolframite, and precedes sulphide
307 deposition (sphalerite, pyrrhotite, chalcopyrite), which characterises stage III. All other
308 minerals found in the topaz veins belong to later stages, and replace locally and partially
309 euhedral topaz crystals: muscovite, arsenopyrite, and chlorite (Carocci, 2019).

310 At the exception of isolated topaz-pyrrhotite veins, stages II and III most often correspond to
311 the opening of fractures within earlier vein systems from stage I. The reopening may occur
312 anywhere, either at the boundaries or in the central part, of the previous vein. The successive
313 openings are not necessarily parallel, and indeed they rarely are. Intense
314 dissolution/replacement processes accompany the opening during Stage III.

315

316 **4.2. Fluid inclusions results**

317 *Fluid characterisation*

318 Table 1 summarises the microthermometric data obtained on fluid inclusions studied in quartz
319 I and topaz from the whole mineral sequence. No reliable inclusions could be identified,

320 unfortunately, in Quartz II. Table 2 shows the representative calculated bulk compositions and
321 corresponding microthermometric and Raman data of the selected fluid inclusion types. The
322 predominant type consists of aqueous-carbonic fluid inclusions that can be further subdivided
323 into three sub-types:

324 - Lc-w inclusions are aqueous-carbonic fluid inclusions whose volatile phase homogenises to
325 the vapour phase (Th CO₂) and whose total homogenisation (Th) occurs into the liquid
326 aqueous phase; their volumetric fraction of the volatile phase (fvp) ranges from 20 to 30%.

327 - Lw-c inclusions are aqueous-carbonic fluid inclusions with an fvp of around 30%, and the Th
328 CO₂ is not observable. Some of them show a Tm CO₂, a clathrate melting temperature (Tm
329 cl), and total homogenisation (Th) to the liquid phase.

330 - Lc-(w) inclusions are high-density carbonic-aqueous inclusions dominated by volatiles, with
331 an fvp higher than 90%. The nucleation of clathrates also reveals water. They homogenise into
332 the liquid carbonic phase.

333

334 Quartz I: Aqueous-carbonic fluid inclusions are the predominant inclusions. Quartz I domains
335 are full of inclusions and are surrounded by a later clear quartz corresponding to recrystallised
336 areas during an unknown stage, probably later than the three first stages (Fig. 8 a, b, and e).
337 In quartz I (and II), most fluid inclusions are affected by deformation (Fig. 8a and b). The largest
338 FIs are highly irregular, with dendritic textures indicating stretching and re-equilibration (Vityk
339 and Bodnar, 1995, Diamond, 2003) processes under ductile conditions (Fig. 8 c and d). Most
340 of them are empty. The boundary between inherited Qtz I and clear quartz is generally difficult
341 to establish (Fig. 8 a, e and f). In Qtz I, close to clear quartz, a few smaller deformed Lw-c fluid
342 inclusions are dispersed. The remaining FI content shows significant variability in the
343 volatile/water ratio and CO₂/CH₄ ratio (Fig. 8f). The melting temperature of CO₂ (Tm CO₂)
344 ranges from - 60.8 to -58.1°C (Table 1). Tm cl ranges from 5.3 to 10.1 °C and Tm ice from -
345 7.8 to -4.6 °C. Total homogenisation temperatures range from 198 to 232°C. In clear quartz,
346 fluid inclusions are frequently absent (Fig. 8e). Inclusions from quartz Qtz II, could not be
347 studied due to their too small size or contorted shape.

348 Topaz I and II: Comb topaz in veins is consistently polyphase. A first-generation (Toz I) is
349 clouded by decrepitated or deformed inclusions (Fig. 9a to c), having lost their fluid content
350 and may present evidence of plastic deformation. The overgrowing rims (Toz II) are never
351 deformed, close to sulphides (Fig. 9 a and b), and contain a lesser quantity (clearer crystals)
352 of preserved fluid inclusions (Fig. 9d). The Toz I to II transition was, therefore, simultaneous
353 with the deposit scale decrepitation event that also affected the early fluid inclusions present
354 in Qtz I and II.

355 The three main types of FI (Lc-w, Lw-c, and Lc-(w)) form distinct FI assemblages in topaz II
356 (Fig. 10a). Clusters of Lc-w FI dispersed in clear topaz constitute the first FI assemblage (FIA)

357 and may be considered as primary FI. Small fluid inclusions planes (FIP) contain Lc-(w) FIA.
358 The latter can be regarded as pseudo-secondary inclusions following the terminology of
359 Roedder (1979) and Bodnar (2003). These FIPs do not crosscut Toz I, for instance, and their
360 extension is limited to parts of Toz II (Fig. 10a to 10d).

361 The first FIA Lc-w inclusions (Fig. 10b) are of 15 to 30 μm in size and showed fvp ranging from
362 20 to 30 vol.%. $T_m \text{CO}_2$ ranges from -61.7 to -57.4 $^\circ\text{C}$, $T_h \text{CO}_2$ (L+V \rightarrow V) ranges from 10.6 to
363 19.4 $^\circ\text{C}$ (Table 1). $T_m \text{cl}$ ranges from 6.1 to 9.8 $^\circ\text{C}$ and $T_m \text{ice}$ from -6.9 to -4.4 $^\circ\text{C}$. Total
364 homogenisation temperatures for Lc-w inclusions range from 250 to 295 $^\circ\text{C}$.

365 The second FIA characterised by Lw-c inclusions (Fig. 10 c) does not show visible $T_h \text{CO}_2$.
366 $T_m \text{CO}_2$ is observed only in a few inclusions between -61.7 and -58.4 $^\circ\text{C}$ $T_m \text{cl}$ ranges from 5.1
367 to 8.4 $^\circ\text{C}$; $T_m \text{ice}$ from -6.9 to -4.3 $^\circ\text{C}$ and T_h from 245 to 255 $^\circ\text{C}$.

368 The third FIA is represented by carbonic (-aqueous) fluid inclusions (Lc-(w)) (Fig. 10d). These
369 FI are 15 to 40 μm in size and often display a crystal negative shape (Fig. 10d). They are one-
370 phase or two-phase FI (Fig. 10d) at room temperature. Thus, water can occur either as a thin
371 meniscus up to 10 vol.% of the fluid inclusion volume (Lc-(w)) or is not visible in smaller
372 inclusions (apparent Lc); clathrate melting reveals the presence of small water amounts. At
373 room temperature, the fraction of the volatile phase (fvp) ranges from 90 to 100 vol.%. $T_m \text{CO}_2$
374 of these inclusions ranges from -60.0 to -58.7 $^\circ\text{C}$, $T_h \text{CO}_2$ (L+V \rightarrow L) are identical for a given
375 cluster and ranges from 10.3 to 12.5 $^\circ\text{C}$. $T_m \text{cl}$ ranges from 8.6 to 9.8 $^\circ\text{C}$ and $T_m \text{ice}$ from -7.1
376 to -4.9 $^\circ\text{C}$. Total homogenisation temperatures range from 289 to 312 $^\circ\text{C}$.

377 In both Lc-w and Lw-c, CO_2 predominates in the volatile phase (82 to 95 mol.%), the CH_4
378 content ranging from 2 to 9 mol.% and N_2 from 6 to 9 mol.%. In Lc-(w) inclusions, N_2 ranges
379 from 9 to 13 mol.% (Table 2), and CH_4 ranges from 2.7 to 3.7 mol.%. Table 2 provides the
380 main features of representative FI bulk compositions.

381

382 **Bulk chemical evolution**

383 Water is the main constituent of the aqueous-carbonic fluids (Lc-w) from Qtz I and II. The
384 partial resetting of the FI during deformation may explain variations in density and
385 volatile/water ratio ranges shown in Fig. 11. In topaz II (Stage IIIa), water-rich aqueous
386 carbonic FI and volatile-rich liquids constitute two assemblages of FI characterised by high
387 densities and well-defined chemical compositions. Both have a volatile component dominated
388 by CO_2 and a minor CH_4 contribution, but differences in the N_2 content (Fig. 12).

389 All fluid inclusions from I-II and III stages are aqueous-carbonic and have $\text{H}_2\text{O}/\text{CO}_2/\text{CH}_4$ ratio
390 close to those predicted by water-graphite equilibrium at high temperatures above 400 $^\circ\text{C}$
391 (Huizenga, 2001). The volatile phase, dominated by CO_2 , from both the Lw-c and Lc-w
392 inclusions, is coherent with the high P-T pair of trapping at water-graphite equilibrium, as
393 discussed below. Thus, two trends are distinguished in the diagram N_2/CO_2 versus CH_4/CO_2

394 (Fig. 12): i) the first one at nearly constant CH_4/CO_2 is characterised by a broader range of N_2
395 contents and corresponding to the volatile-rich fluid enriched in N_2 and ii) the aqueous-carbonic
396 fluids (Lc-w, Lw-c) with a CH_4/CO_2 ratio ranging from 0.05 to 0.10. Fig. 11 and 12 emphasise
397 the similarities between Lc-(w) and (Lw-c) FI, distinctively of Lc-w FI. The Lc-w inclusions are
398 slightly richer in N_2 , e.g., a gas produced by the oxidation of ammonium released by micas or
399 feldspars alteration or melting.

400

401 **5. Interpretation and discussion**

402 *5.1. P-T estimation*

403 A series of isochores representative of the different fluid types calculated from
404 microthermometric and Raman spectroscopy measurements are reported on a pressure-
405 temperature plot together with thermal gradients (Fig. 13). The dense volatile-rich carbonic
406 fluids Lc-(w) trapped in topaz have rather flat isochores, sub-parallel to high thermal lithostatic
407 gradients between 50 and 60°C/km. The Lc-w inclusions show much steeper isochores. As
408 Lc-(w) and Lc-w are trapped in the same clear topaz II and considered as sub-synchronous of
409 the same event, the intersection of their isochores provides the best estimates of their trapping
410 conditions. The resulting P-T box 480–520 °C range, and 230–270 MPa, is inferred for the
411 topaz stage, i.e., slightly below P-T conditions (300-350 MPa, 500-550°C) estimated for
412 contact metamorphism developed by late to post-tectonic granites in northern Portugal
413 (Guedes et al., 2002, Noronha et al., 1999, Vallance et al., 2003).

414 The presence of both Lc-(w) and Lc-w fluids, one dominated by volatiles and the other by water
415 could be at first glance interpreted as the product of unmixing. The unmixing is, however, highly
416 improbable considering the P-T estimates above mentioned, which are far from the isopleth in
417 the $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ system. The conditions of unmixing along the isopleth or under lower P-T
418 pairs (two-phase field) in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$, and for salinities around 6 wt % NaCl
419 equiv. (Weisbrod, 1984, Diamond, 2003), are: i) at 200-250 MPa, around 250 to 330°C, e.g.
420 approximately 100 to 150°C below the inferred temperature, and ii) at 500°C, about 60 MPa,
421 thus 150 to 200 MPa below the inferred pressure. Therefore, the unmixing of the volatile phase
422 from a parent aqueous-carbonic fluid can be precluded.

423 The presence of volatile dominated Lc-(w) fluids and aqueous-carbonic Lc-w fluids can be
424 alternately interpreted as fluids generated at two distinct higher temperatures, at equilibrium
425 with graphite. The consideration of the fluid compositions in the C-H-O(N) system in
426 equilibrium with graphite can be used to estimate the P-T conditions along which the fluid
427 composition evolved (Huizenga and Touret, 1999; Huizenga, 2001). Redox conditions need
428 first to be evaluated. Oxygen fugacity ($f\text{O}_2$) values near the quartz-fayalite-magnetite (QFM)
429 redox equilibrium is a reasonable assumption for either high-grade metamorphic rocks or low-
430 grade graphite-bearing metasediments (Ohmoto and Kerrick, 1977; Lamb and Valley, 1984).

431 Under these redox conditions, for the Lc-w fluid, a water content higher than 0.9 and
432 $X_{CO_2}/(X_{CO_2}+X_{CH_4})$ above 0.9 yield to P-T estimates around 450-470°C-220 MPa or above,
433 in agreement with the P-T domain issued for isochore intersection. For the Lc-(w) fluids, a
434 temperature of 550°C and equilibrium water-graphite at QFM, is necessary to explain an $X_{CO_2}/$
435 $(X_{CO_2}+X_{H_2O}+X_{CH_4})$ reaching 0.9, a temperature significantly higher than for Lw-c fluids.
436 Thus, the water content decreases drastically with increasing temperature above 500°C to
437 values around 0.1 (Huizenga, 2001). At such temperature, CH₄ is not supposed to be present,
438 but traces of CH₄ in the Lc-(w) fluid could be related to subsequent contamination during fluid
439 ascent and mixing process. The two main types of fluids could have been thus generated via
440 similar processes and from similar pristine fluids but at two distinct temperatures. The lack of
441 re-equilibration of the ascending Lc-(w) fluids may be due to kinetics and velocity of the fluid
442 ascent. N₂ in the aqueous-carbonic fluids could find its origin in the release of nitrogen during
443 fluid-rock interactions, either from micas or from feldspars where ammonium is substituted to
444 potassium (Bebout and Fogel, 1992, Moine et al., 1994). N₂ is thus rather abundant in fluids
445 issued from migmatites. Graphite-saturated CO₂-N₂ fluid inclusions were found in migmatites
446 formed from metapelites in western Carpathians (Hurai et al., 2000). Nitrogen found in dense
447 carbonic liquids may be related to the oxidation of ammonium from micas or feldspars during
448 fluid-rock interaction or partial melting at depth. CO₂-H₂O fluids were found in a variety of
449 migmatites formed from metasedimentary sequences. For instance, migmatites from Terra
450 Nova Bay developed under 35 MPa, and 700°C present such fluid types (Giorgetti et al., 1996).
451 It is, therefore, reasonable to infer the existence of a migmatitic zone to produce a large volume
452 of fluids similar to those encountered at Panasqueira.

453 Considering the few isochores available for the densest fluid inclusions from quartz Qtz I, a
454 rough estimate of the Qtz I formation is around 430-500°C and 210-290 MPa. Pressure
455 fluctuations may have occurred due to oscillations around lithostatic pressures. The structural
456 level estimated for the topaz stage is around 8 to 10 km depth. Such a depth is not surprising
457 when considering the whole CIZ. Noronha et al. (1992, 1999) proposed similar pressure for
458 most other W deposits from northern Portugal. Pseudo-metamorphic fluids equilibrated with
459 metamorphic rocks are recorded in most Au deposits from western Europe (Boiron et al., 1996,
460 2003) and found abundantly in As-Au deposits from the CIZ in north-Portugal and trapped as
461 such pressures (Vallance et al., 2003).

462 These high pressures and deep structural levels contribute to a new vision of the hydrothermal
463 system at Panasqueira. Thus, unlike most previous works (references in the introduction) that
464 followed Kelly and Rye's model of a magmatic-hydrothermal fluid system linked to a shallow
465 granitic intrusion at a depth of less than 3 km, the data obtained in the present work
466 demonstrate that the W-deposit results from non-magmatic fluids flowing at a depth of about
467 8-10 km. Such depth for Stages I-II and III is likely related to a period prior to exhumation.

468 Taking into account the ages available at the beginning of the hydrothermal system dated by
469 U-Pb on W-rich rutile (305.2 ± 5.7 Ma, Carocci et al., 2020) and cassiterite (303 to 301 Ma,
470 Zhang et al., 2019), the most probable age for this period is 301-306 Ma..

471

472 *5.2 Wolframite and quartz-topaz deposition*

473 According to our findings, the main stage of W deposition was a quasi-monomineralic stage
474 characterised first by the predominant deposition of wolframite at the fracture edges, and the
475 sealing of the vein by quartz, as in most W deposits worldwide, such as the W-veins from the
476 main Chinese W province (e.g., Liu et al., 2018). Topaz infilled specific fractures, and
477 sometimes sphalerite and pyrrhotite end the infilling. During the topaz stage, two fluids are
478 present: a dense volatile (CO₂)-dominated liquid enriched in N₂ and an aqueous-carbonic fluid.
479 Both fluids may result from the equilibrium between water and graphite at different
480 temperatures within the metamorphic series. They display similarities with the rare relics from
481 stage I tungsten depositing fluids. Gibert et al. (1982) have shown by modelling that the
482 addition of less than 10 mol.% N₂ to the mineralising fluids results in a marked increase in
483 H₂WO₄ and HWO₄⁻ concentrations relative to WO₄²⁻ and subsequently yield a significant
484 decrease of W-mineral solubility. Pulses of volatiles (N₂, CH₄, CO₂) affect the dielectric
485 constant of water and favour subsequently W-mineral precipitation. Such a process accounts
486 for the commonly observed association of W-deposits with graphitic series generating volatiles.
487 The origin of nitrogen may either be related to the oxidation of ammonium contained by micas
488 or feldspars within metamorphic series, or to the release of N₂ during the partial melting of
489 feldspars and micas in the migmatites at depth.

490 After wolframite deposition, pressure fluctuation produced by a fault-valve process (Sibson
491 1990, 2000) may finally explain the massive quartz deposition. This model was already
492 proposed by Foxford et al. (2000), who considered the vein swarm as formed through
493 extensional failure driven by hydraulic-valving. Quartz deposit is favoured at constant
494 temperature by pressure drop-down consecutive to the failure, as quartz solubility decreases
495 together with pressure decrease (Fournier, 1983). The formation of sulphides after topaz is
496 more challenging to explain, in particular the sudden venue of H₂S rich fluids enriched in Zn
497 and probably Fe. This point will not be discussed here, having been cogently addressed by
498 Kelly and Rye (1979).

499

500 *5.3 Deep-seated heat anomalies and fluid sources*

501 The P-T domain delineated by isochores suggests high thermal gradients of 50 to 60°C /km
502 (Fig. 13) which are higher than the regional 42°C/km gradient for Upper Carboniferous (e.g.
503 Ferreira et al., 2019). Besides, a part of the fluids (Lc-(w)) equilibrated with host metamorphic

504 formations at a higher temperature than at the deposition level (Fig. 14). Therefore, heat
505 advection was involved.

506 The main Panasqueira granite intruded the Beira schist before the inception of the
507 hydrothermal system as the thermal aureole assemblages were obliterated by the early
508 tourmalinisation (Carocci et al., 2020). It cannot, therefore, be the required heat source.
509 Quartz-wolframite veins then intersected the later rare metal granite sequence found in the
510 "Greisen cupola" (Marignac et al., 2020), indicating that granites could not be considered as a
511 heat source either. However, the presence in the SW of the deposit of both the topaz rich (\pm
512 cassiterite) zone and the geophysical anomalies at close distance (Fig. 2) likely testify for the
513 presence of concealed intrusions responsible for Sn and F inputs (Pinto et al., 2015). Such
514 intrusions would be of too small volume and could have been at best only additional sources
515 of heat.

516 On the other hand, high-temperature events are documented in the lower crust of the CIZ
517 during all the Late Carboniferous (Orejana et al., 2011), implying the long-lasting possibility of
518 heat advection by upward fluids transfer. Migmatites domes are known in several places in the
519 CIZ, in particular in the Spanish Central System, to the east of the Panasqueira area (Fig. 2).
520 A first migmatisation event, yielding banded metatexites, was widespread and occurred at c.
521 320 Ma (e.g., Lopez-Moro et al., 2018). A second event, more localised in the core of D3
522 domes, was characterised by biotite dehydration melting yielding cordierite-bearing diatexites
523 and occurred at c. 305-300 Ma (e.g., Diaz-Alvarado et al., 2013).

524 A migmatite domain from the second migmatisation event would, therefore, be a likely source
525 of heat, and also of fluids, below the Panasqueira deposit as suggested by the schema from
526 figure 14. Experimental and field data concur in showing that dehydration-melting "granitic"
527 melts contain significant amounts of dissolved water, typically around 5 wt % at 750°C and 500
528 MPa (Le Breton and Thompson, 1988; Braga et al., 2010, Carvalho et al., 2019). Thus, as
529 pointed out by Braga et al. (2010), migmatites produced in a continental collision zone will act
530 as a sink of hydrous fluids as long as the crust is partially molten. Then, upon cooling and
531 decompression towards subsolidus conditions, the fluid stored in the migmatitic leucosome will
532 be released. Given the large volume of migmatite domains, they constitute therefore the most
533 significant potential source of deep fluids in the crust, far more than granites.

534 Besides, as shown in the Ivrea zone, metapelitic migmatites formed through muscovite and
535 biotite breakdown melting may produce C-O-H-N fluids. The latter fluids are assumed to be
536 internally derived by devolatilisation of hydrous silicates in the graphitic protolith, then as a
537 result of oxidation of carbon by melting of Fe³⁺-bearing biotite (Carvalho et al., 2019). Such a
538 process applies to the mechanisms of production of Panasqueira fluids.

539

540 *5.4 Mass and heat transfers from deep levels up to the Panasqueira level*

541 Panasqueira fluids had to travel from the deep-seated zones up to the deposition levels at the
542 top of the Panasqueira granite, at about 10 km depth, e.g. close to the top of ductile-brittle
543 transition zone which occurs around 10 to 16 km depth (Ingebritsen and Manning, 2010, Llana-
544 Funez and Lopez-Fernandez, 2015).

545 Fluid circulation is possible in the deep crust. Large fluid quantities stored in the lower crust at
546 peak metamorphic conditions are later expelled towards shallower crustal levels during
547 retrogradation (Touret and Nijland, 2013). On the one hand, theoretical considerations show
548 that permeability can be significantly enhanced. At depth in the ductile Earth's crust,
549 permeability increases significantly, at strains as low as a few per cent, through microcrack
550 growing and rapid development of connectivity in grain-scale crack networks. Thus, the pore
551 fluid factor, which is the ratio of pore fluid pressure to vertical stress, is high enough to facilitate
552 deformation by microcracking (Conolly, 1997; Cox, 2002). Indeed, in zones characterised
553 generally by a permeability as low as 10⁻¹⁸-10⁻²⁰m², permeable vertical cracks can efficiently
554 transfer heat energy, magmas and fluids from the lower crust to the upper crust (Ingebritsen
555 and Manning, 2010, Zhao et al., 2002). On the other hand, there is plenty of field evidence that
556 metamorphic fluids may migrate towards deep shear zones where they are focused and may
557 flow upward (e.g., Van Reenen et al., 1994, Kolb et al., 2004, Siebenaller et al., 2013, Rolland
558 and Rossi, 2016, Dya-Person et al., 2018).

559 In the Panasqueira case, there is no direct evidence for the existence of a drainage zone.
560 Nevertheless, indirect evidence seems to testify for a permanent structure allowing recurrent
561 transfers of fluids and magmas. First, the late-kinematic "Seixo Bravo" quartz veins which
562 prove for metamorphic fluid circulation (Noronha et al., 1992) were only found within the
563 Panasqueira area, where they form a subvertical cylindrical volume, suggestive of a deep-
564 rooted subvertical fluid pathway (Fig. 14). Field observations demonstrate that the Seixo-Bravo
565 veins predated the Panasqueira granite emplacement (Noronha et al., 1992; Launay, 2018).
566 Second, there is a need for a pathway for the magma, which resulted in the main Panasqueira
567 granite laccolith emplacement. Feeding through vertical dykes is the commonly accepted way
568 for such an emplacement (Petford et al., 2000) and indeed, geophysical modelling (Ribeiro,
569 2017) shows the existence of NE-SW root that may be related to such a dyke. Third, the
570 recurrence of rare metal granite emplacement (Marignac et al., 2020) argues for the
571 persistence of a weakness zone under the deposit, the more if effectively tin and fluor of stage
572 III must be related to a new input of rare metal magma. Ascent of magmas are favored by a
573 transpression zone of transcurrent shear, in particular in extensional segments of the
574 associated strike-slip system (Brown, 1994, Brown, 2013). Finally, the isotopic ratio of helium
575 ³He/⁴He trapped in FI from wolframite (Burnard and Polyá, 2004) is five times higher than the
576 atmospheric ratio and, therefore, inconsistent with a peraluminous granite source. These
577 authors thus interpret fluids as coming from a deeper source such as migmatites, or the mantle.

578 This conclusion is a further argument for a deep-seated structure, similar to those
579 demonstrated in the Great Basin (Nevada, USA) by Siler and Mack Kennedy (2016).

580

581 *5-5 Fault valve behaviour in the lower part of the seismogenic region*

582 Whereas fluid flow is continuous along actively creeping parts of shear networks, in contrast,
583 at and above the seismic-aseismic transition, potentially significant, cyclic changes in fault
584 permeability are associated with episodic rupture and interseismic fracture sealing (Cox,
585 2002). Such fracture development follows the classic fault-valve process (Sibson, 1994;
586 Boullier and Robert, 1992, Kolb, 2008). It is in the lower regions of the seismogenic zone, i.e.
587 around 10 km depth like at Panasqueira, that valve-action is the most effective (Sibson, 1992,
588 1994). There, large ruptures tend to nucleate as a consequence of fluid overpressure, as
589 proposed for the Panasqueira vein system (Foxford et al., 2000). Fluctuation around lithostatic
590 pressure during the topaz stage fits well with this model.

591

592 **6. Conclusion**

593

594 - The oxide stage at Panasqueira is a quasi-monomineralic stage characterised by the
595 predominant deposition of wolframite at the fracture edges, and the sealing of the vein by
596 quartz, as in most W deposits worldwide. The topaz stage occurs after W deposition during a
597 stage characterised by the reopening of the boundary between the vein and wall rock or new
598 fracture infilling crosscutting wolframite.

599 - At variance of Qtz I and Topaz I which underwent a deformation causing the almost complete
600 loss of the primary fluid inclusions, the topaz II hosts high-density liquids either aqueous-
601 carbonic or volatile-rich which indicate trapping conditions of $500 \pm 20^\circ\text{C}$ and $240 \pm 20 \text{ MPa}$.
602 Thus, unlike most previous works that followed Kelly and Rye's model of a magmatic-
603 hydrothermal system linked to a shallow granitic intrusion (less than 3 km), the data obtained
604 in the present work demonstrate that the main fluids percolating the vein system at a depth of
605 about 8-10 km, were non-magmatic, rooted at greater depth, and deeply equilibrated with
606 metamorphic formations.

607 - the high thermal gradient in between 50 and $60^\circ\text{C}/\text{km}$, the successive granite intrusions
608 including rare-metal granite acting as a source of F and Sn, the previous formation of
609 subvertical and deformed quartz veins (Seixo Bravo veins), the presence of fluids equilibrated
610 at higher temperatures attest for a long-lived upward transport of magmas and fluids from the
611 deeper crust. A hypothetical deep crustal shear zone, located below the deposit, is proposed to
612 explain the upward circulation of waters possibly extracting tungsten from either the
613 metamorphic series or previously crystallised granites or both. The wolframite and then the
614 topaz deposition occurred probably when the structural level was at the basis of the

615 seismogenic zone, thanks to fault-valve fracturing and sealing processes, at the beginning of
616 the exhumation of the CIZ belt, probably around 301-306 Ma.

617

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628

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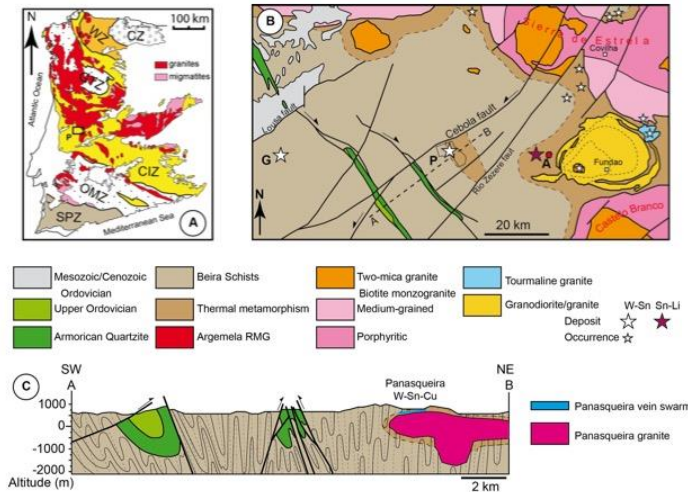


Fig. 1

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911 Fig. 1: A) Simplified geological map of the Variscan Iberian massif with the location of the Panasqueira deposit
 912 district (noted P) within the CIZ (Central Iberian Zone), granites, and migmatites, WZ: West Asturian Leonese Zone,
 913 OMZ: Ossa Morena Zone, SPZ: South Portuguese Zone; B) Regional geological map with indication of the
 914 underground mine (star P), the contact metamorphic aureole (brown) and regional geological outcropping granites.
 915 A: Argemela granite, G: Gois W-showing (data source: Beralt Tin & Wolfram S.A., Jaques and Pascal, 2017,
 916 Jacques et al., 2017, a geological map of Portugal at 1/ 1 000000 (Carta geologica de Portugal, 2016); C: cross-
 917 section (dashed line A-B from map B) with the indication of the Panasqueira laccolith, Panasqueira vein swarm,
 918 and location of the remaining quartzites above the Beira schist formation. (figure slightly modified from Marignac et
 919 al., 2020)

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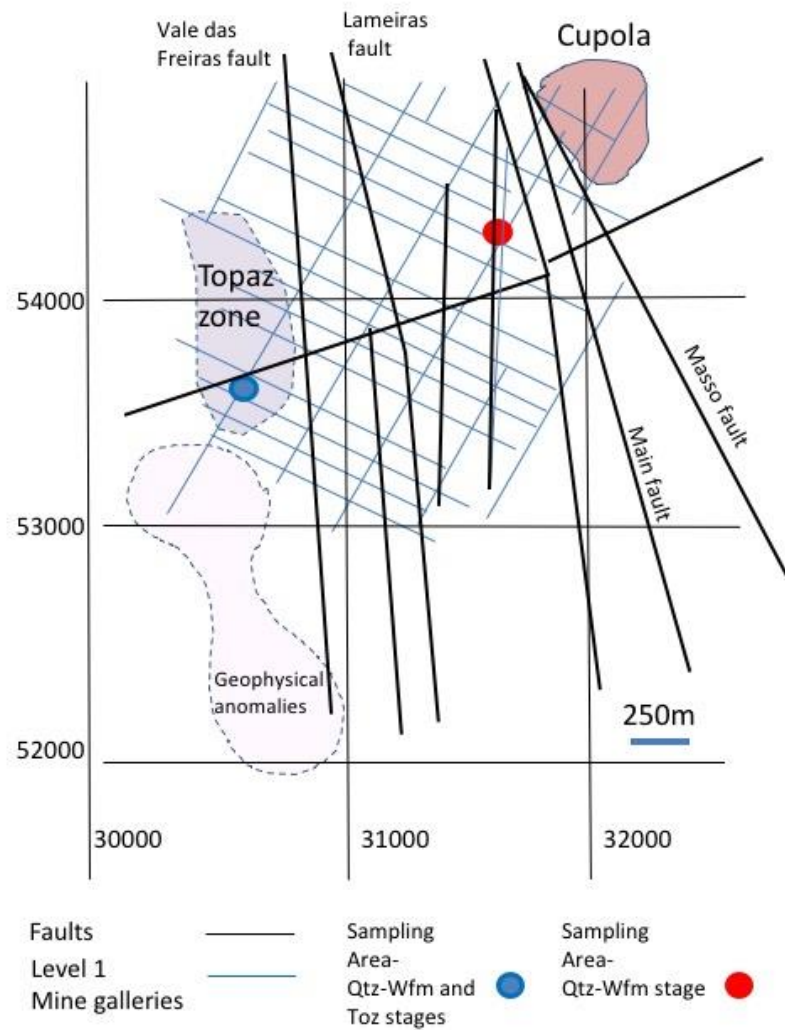


Fig. 2

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 922 Fig. 2: Mine works at Panasqueira (plan view) with an indication of a granite cupola outcropping
 923 at depth in mine galleries, as well as inferred granite bodies from geophysics. Samples are
 924 coming from two main zones: the “topaz zone” in light purple (blue point for sampling zone)
 925 and the “bank” at level 1 (red point) considered as one of the richest zones in W of the deposit.
 926 Qtz: quartz, Toz: topaz, Wfm: wolframite.

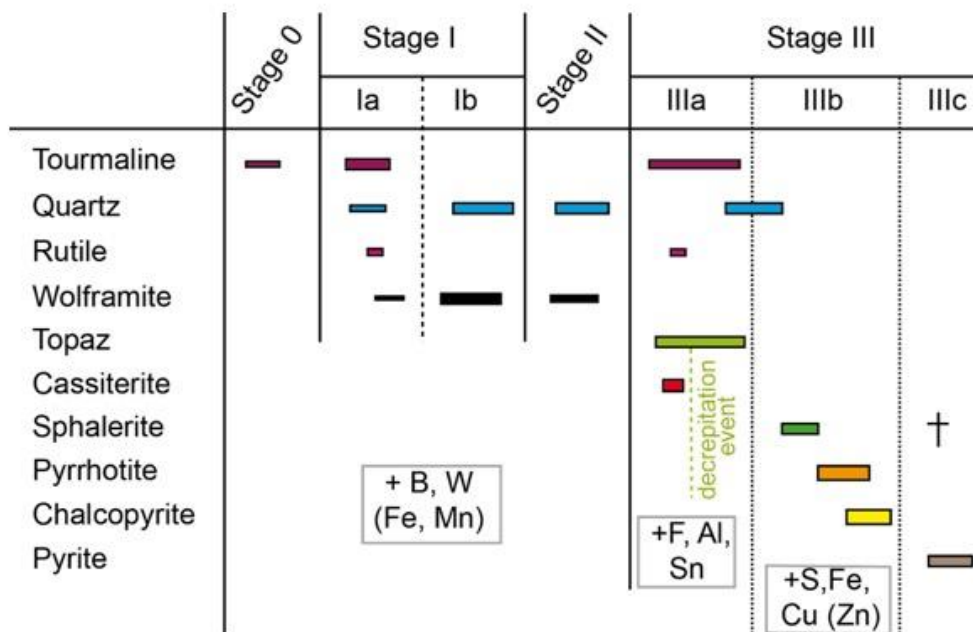


Fig. 3

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928 Fig. 3: Paragenetic sequence of the main stages of W deposition (Stage I-II) and topaz-
 929 sulphides (stage III). The main element associations are indicated in the boxes.

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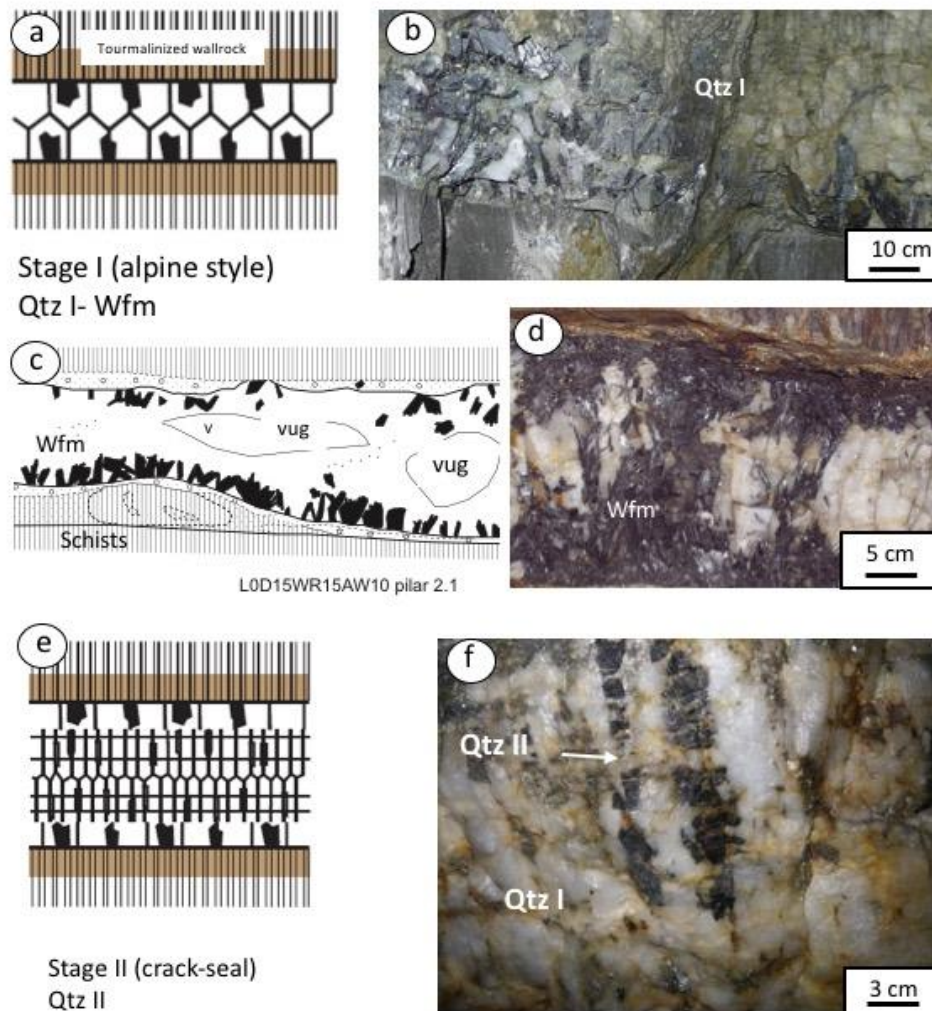


Fig. 4

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934 Fig. 4: Schematic drawings and photographs taken in mine galleries illustrating the stage I-II quartz-wolframite
 935 veins. Wall rocks are affected by tourmalinisation (a), and euhedral wolframite is crystallised along the vein edges
 936 and was followed by massive quartz precipitation, as shown in b, c, and d. Stage II is characterised by the
 937 deformation of quartz I and wolframite, and crack seal fracturing with Qtz II crystallisation (e-f). Qtz: quartz, Wfm:
 938 wolframite.

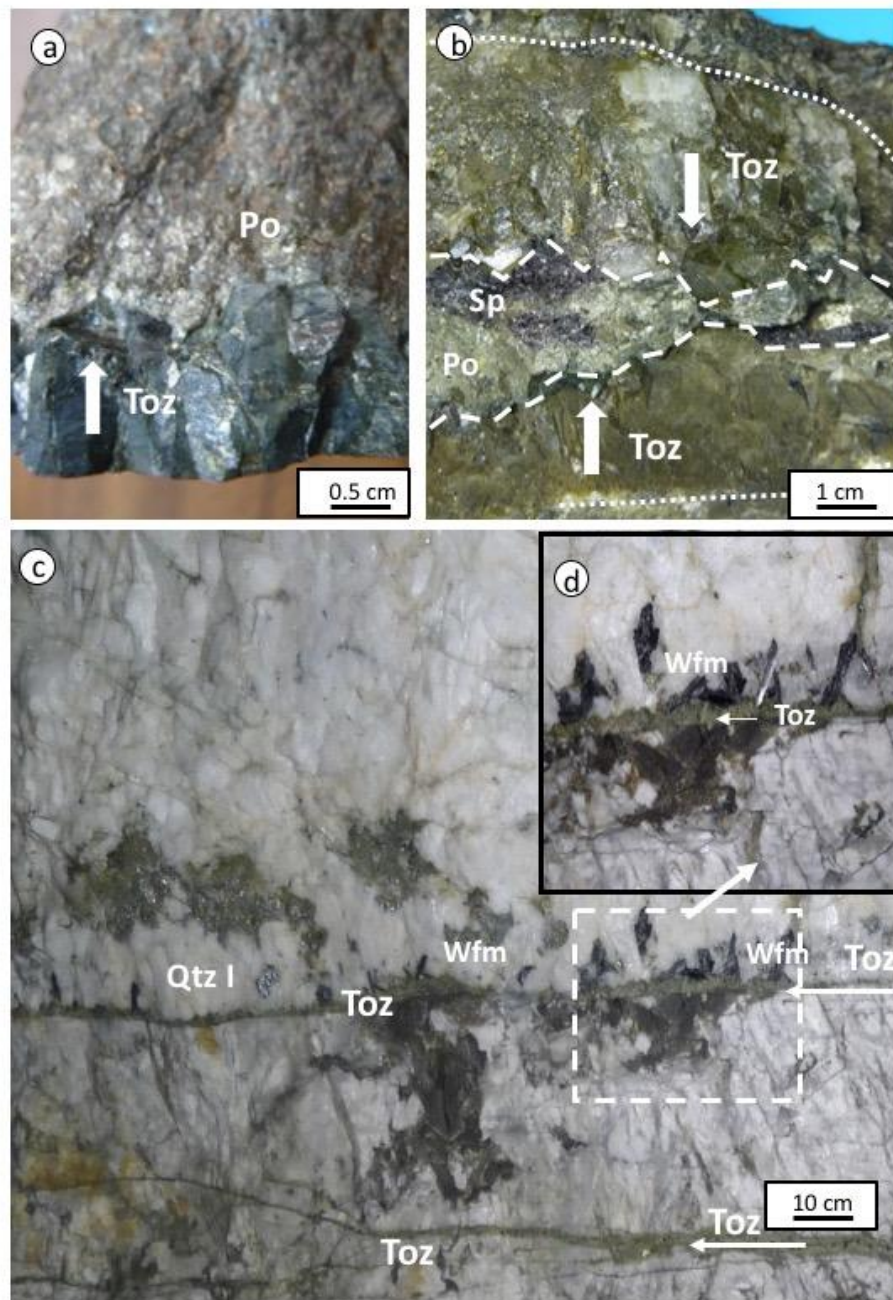


Fig. 5

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940 Fig. 5: Photographs of the topaz veins: a) Euhedral topaz (Toz) vein along vein edges with pyrrhotite
 941 (Po) infilling in the centre of the vein, white arrows indicate the direction of crystallisation, b) Topaz vein
 942 with late sphalerite (Sp)-pyrrhotite infilling in the middle of the vein, c) Thin topaz veins crosscutting the
 943 early assemblage (quartz-wolframite from Stage I-II). d) inset from c) shows a detail of the relationships
 944 between topaz and wolframite.

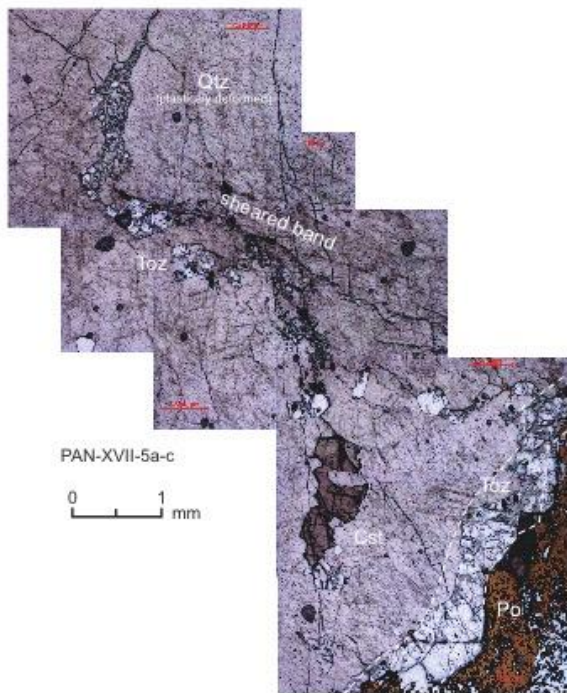


Figure 6

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946 Fig. 6: Microphotograph of topaz along ductile micro-shear showing band the following
947 succession (transmitted light): Quartz I (QtzI), association topaz (Toz) -cassiterite (Cst) as
948 patches developed in Qtz I, topaz veinlet, and then final pyrrhotite (Po) infilling.
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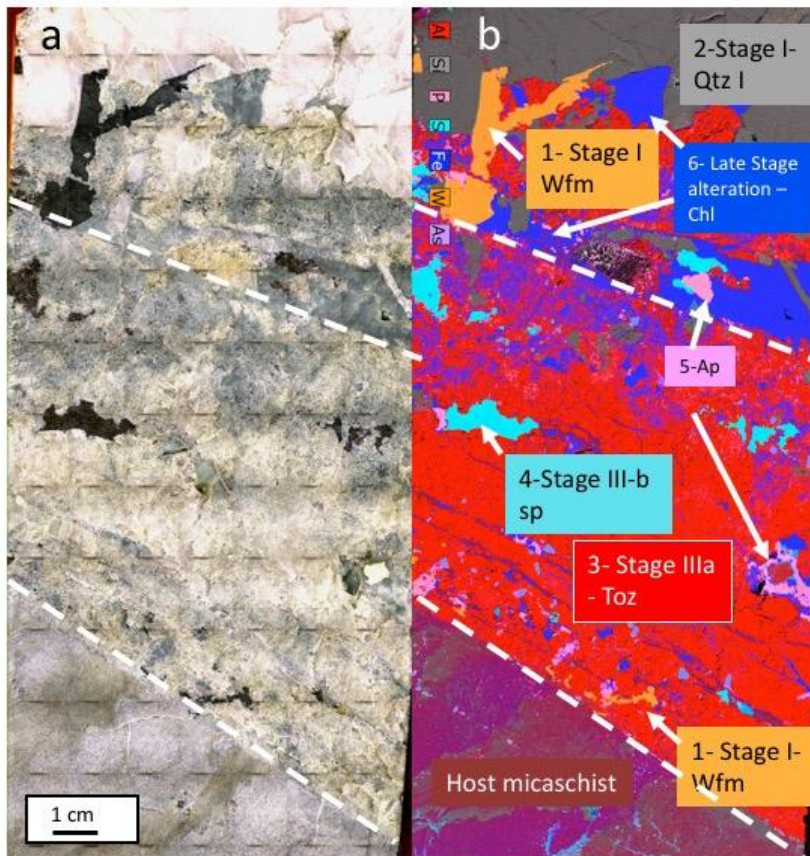


Figure 7

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953 Fig. 7: Example of reopened quartz-wolframite vein boundary with the host micaschist followed by topaz infilling. a)
 954 photograph of the vein, b) micro-XRF element map (Al, Si, P, S, Fe, W, As) of the same sample and mineral
 955 distribution based on chemical element relative abundances: W (Wolframite: Wfm, W), Si (Quartz: Qtz, Si), Al
 956 (Topaz: Toz, Al), S (Sphalerite: Sph, Zn), P (Apatite: Ap, P), Fe (Chlorite: Chl, Fe-Si). Topaz is, in this sample,
 957 affected by later on alteration, in particular a replacement by Fe-chlorite. Wolframite is fragmented and embedded
 958 in topaz.

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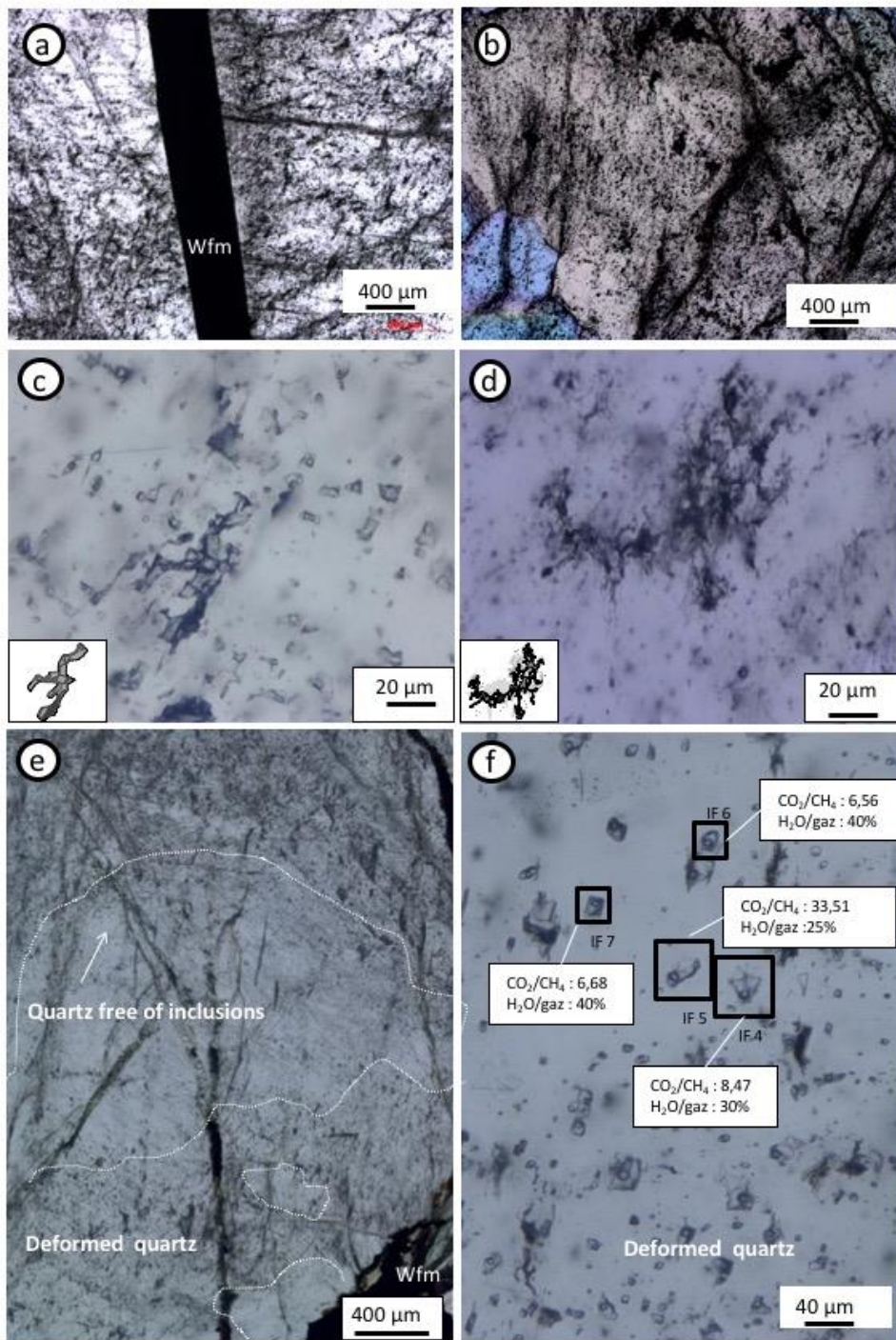


Figure 8

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962 Fig. 8: Microphotographs of Stage I fluid inclusions in quartz QI (transmitted light). a) abundant
 963 decrepitated fluid inclusions close to wolframite in quartz Qtz I, b) deformed quartz Qtz I with
 964 clouds of decrepitated inclusions, c) and d) contorted fluid inclusions in quartz Qtz I, e) clear
 965 quartz domain within Qtz I identified by decrepitated inclusions, f) fluid inclusions with an
 966 indication of their CO₂/CH₄ ratios in the deformed Qtz I.

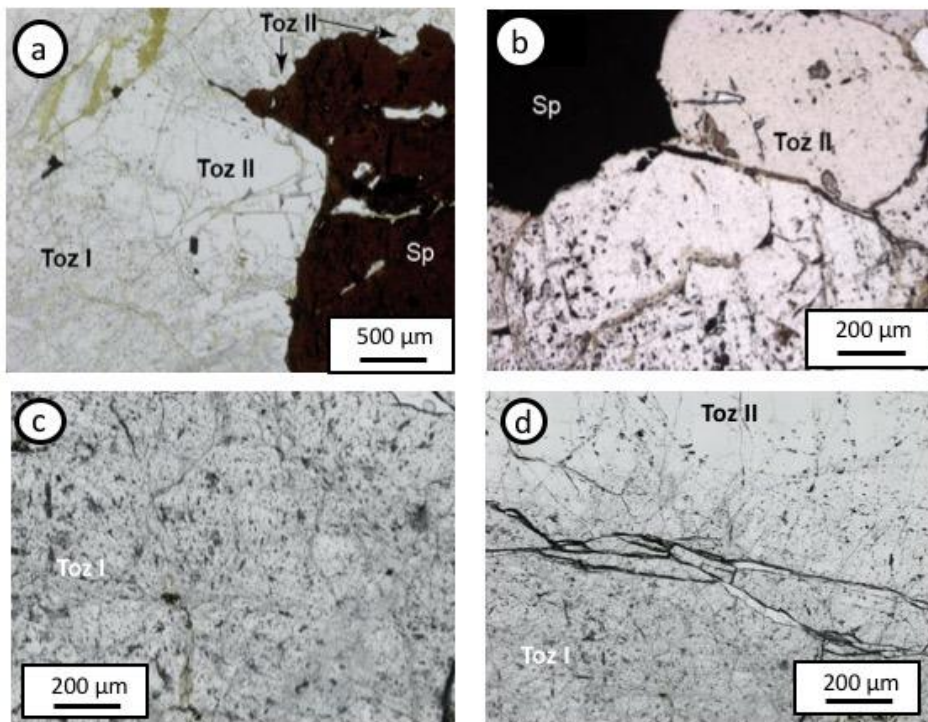


Fig. 9

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968 Fig. 9: Microphotographs showing the fluid inclusion distribution in topaz: a) topaz overgrowth
969 (Toz II) onto topaz I full of decrepitated inclusions (Toz I); b) clear Toz II in contact with
970 sphalerite (Sp); c) detail of the decrepitated inclusions in Toz I, d) contact between Toz I and
971 Toz II.

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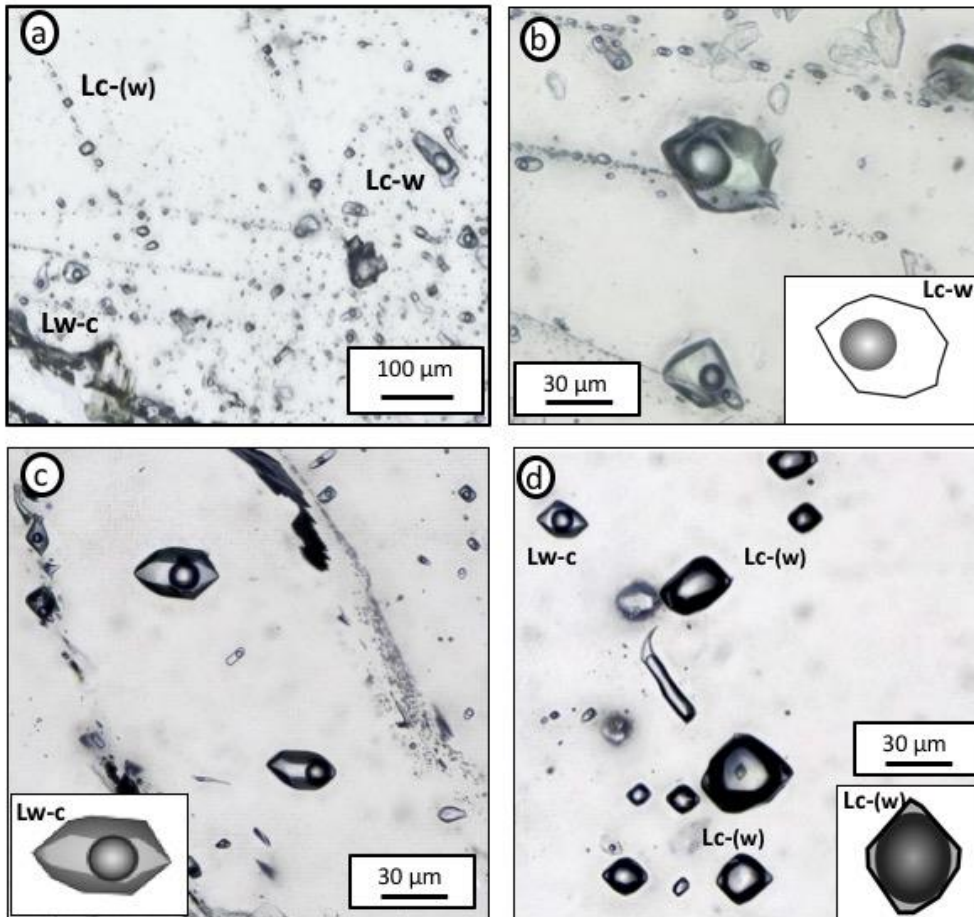


Figure 10

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975 Fig. 10: Microphotographs of fluid inclusions types in topaz II: a) distribution of the three FI
 976 types, Lw-c, Lc-w, and Lc-(w) in Toz II.), b) Lc-w inclusion; c) Lw-c inclusions, d) Lc-(w)
 977 inclusions in a pseudo-secondary plane.

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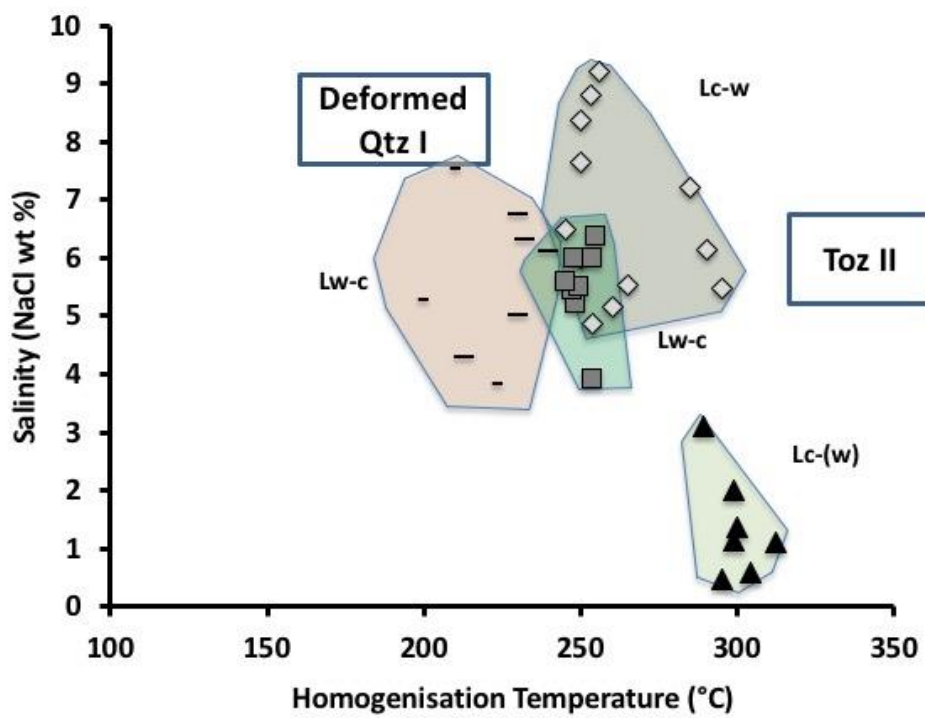


Fig. 11

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981 Fig. 11: Th versus salinity plot for fluid inclusions types found in Topaz (Lw-c, Lc-w, and Lc-

982 (w)) and Quartz I.

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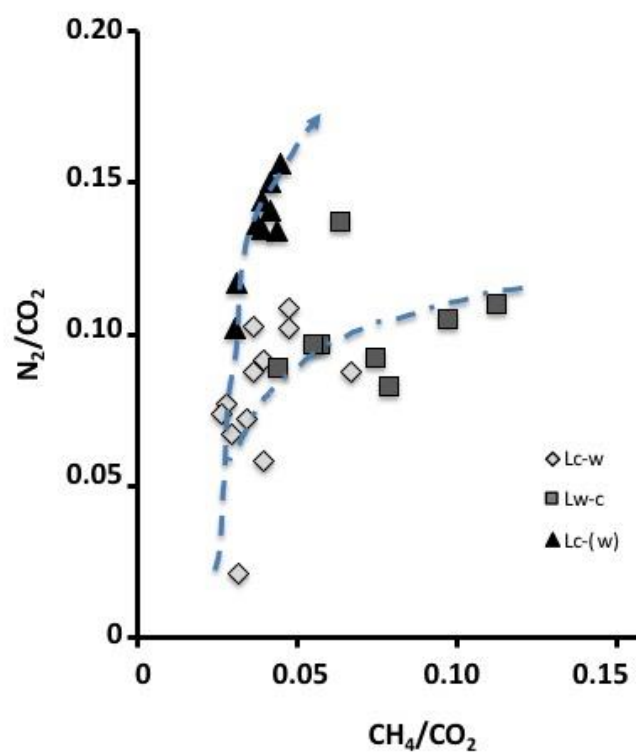


Fig. 12

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987 Fig. 12: N_2/CO_2 versus CH_4/CO_2 plot for the volatile phase of the fluid inclusions types found
988 in topaz.

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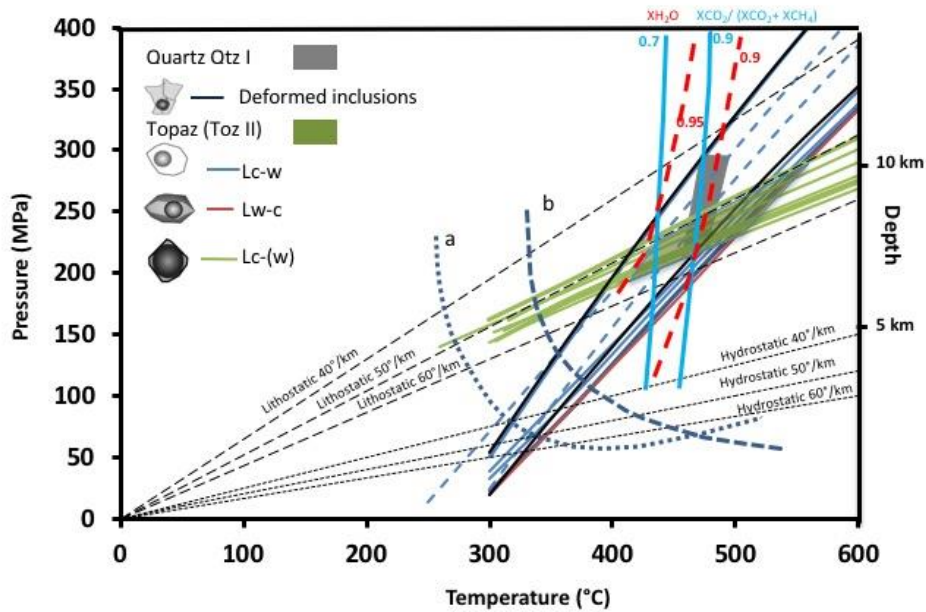


Fig. 13

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993 Fig. 13: P-T diagram for stages I-II and III (Topaz II) at Panasqueira, with isochores of typical inclusions from each
 994 fluid inclusion type. Green box corresponds to the estimated pressure-temperature for the two stages. Isoleths for
 995 XH₂O (thick red dashed lines) and XCO₂/(XCO₂+XCH₄)(thick blue lines) at fO₂ QFM (quartz-fayalite-magnetite) are
 996 from Huizenga (2001). Isoleths (dotted dark blue lines) in the system H₂O-CO₂-NaCl are from Weisbrod (1984)
 997 for a salinity of 6 wt. % NaCl equiv., and a CO₂ content of 10 (a) and 20 (b) mole%.

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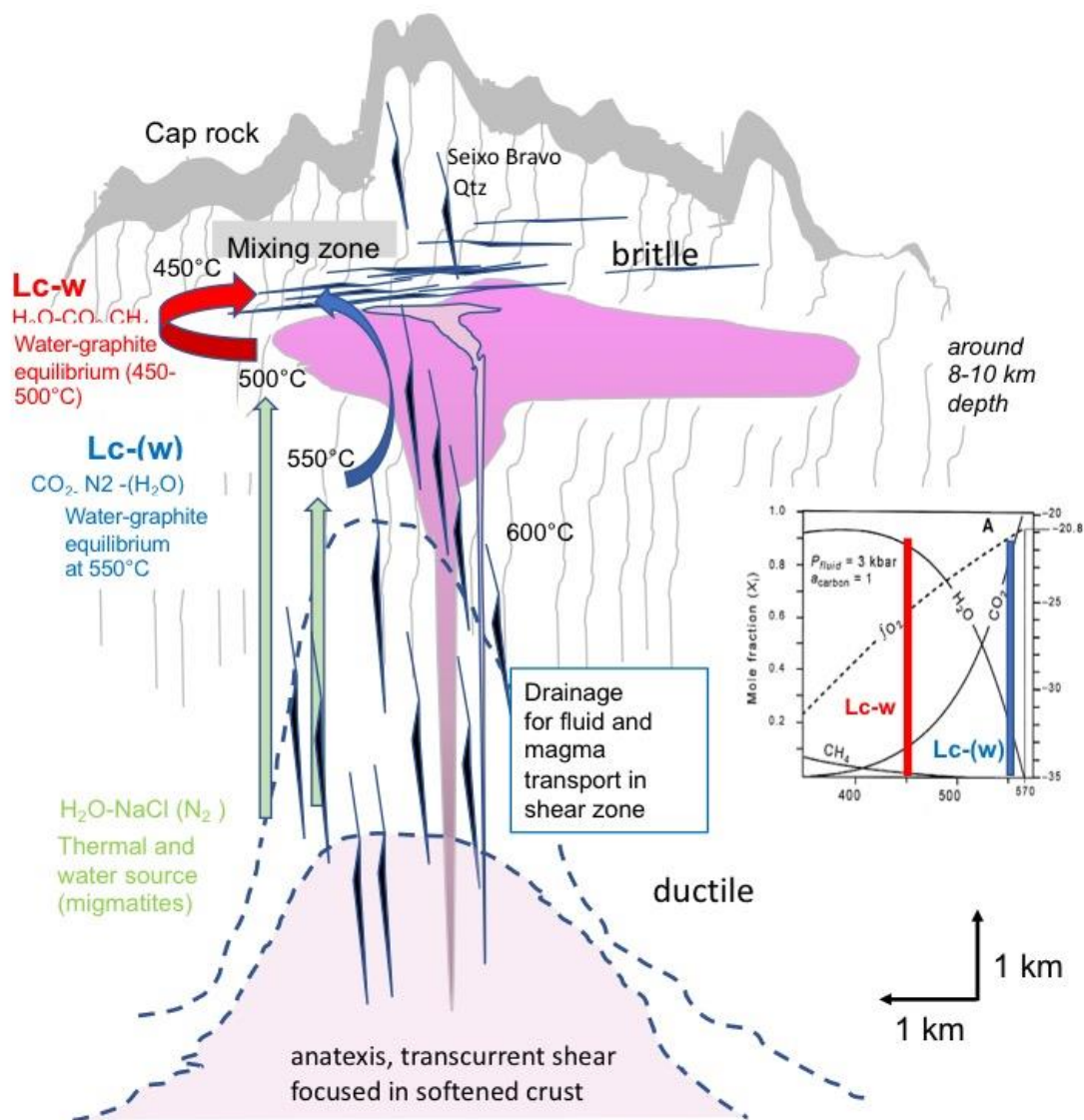


Fig. 14

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Fig. 14: Sketch diagram of fluid circulation and mixing at Panasqueira with three postulated fluid sources: Deep-seated aqueous fluid source from likely anatectic domain, with medium salinity and significant N₂ concentrations, fluids close to equilibrium with graphite at high temperatures above 550°C yielding to the Lc-(w) fluids, and fluids generated at 450-500°C (Lc-w fluids). Mixing is inferred to occur in the sets of joints above the Panasqueira pluton. Late intrusions yielding to the formation of sills at the top of the Panasqueira granite are represented in pink. Inset showing T-X diagram with XH₂O, XCO₂, and XCH₄ in equilibrium with graphite under QFM fO₂ buffer as a function of temperature from Huizenga (2001): red line corresponds to the conditions of genesis of the Lc-w fluids and the blue line of the Lc-(w) fluids.

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Table captions

| Mineral | FI type | Tm CO ₂ | Th CO ₂ | mode | Tm CI | Tm ice | Th | mode |
|----------|---------|----------------------|--------------------|------|-------------------|--------------------|------------------|------|
| Quartz I | Lw-c | -58.1 to -60.8 4 | | | 5.3 to 10.1 14 | -4.6 to -7.8 14 | 198 to 232 6 | L |
| Topaz | Lc-(w) | -58.7 to -60.0 9 | 10.3 to 12.5 9 | L | 8.6 to 9.8 9 | -4.9 to -7.1 7 | 289 to 312 7 | V |
| | Lc-w | -57.4 to -61.7 16 | 10.6 to 19.4 9 | V | 6.1 to 9.8 16 | -4.4 to -6.9 16 | 250 to 295 16 | L |
| | Lw-c | -58.4 to -61.7 3 | | | 5.1 to 8.4 8 | -4.3 to -6.9 8 | 245 to 255 8 | L |

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Table 1: Summary of the microthermometric data for Quartz I and Topaz II (first line: range, second line: number of measurements). L: homogenisation to the liquid phase, V: homogenisation to the vapour phase. See text for other abbreviations. All data are in °C.

| Sample | Zone | Inclusion | Type | Microthermometry (°C) | | | | | | Volatile phase (mole %) | | | | Bulk composition (mole %) | | | | |
|-------------|------|-----------|--------|-----------------------|------|-------------------|-------------------|------|-------|-------------------------|-----------------|-----------------|----------------|---------------------------|-----------------|-----------------|----------------|------|
| | | | | Tm ice | TmCl | TmCO ₂ | ThCO ₂ | Mode | TH | mode | CO ₂ | CH ₄ | N ₂ | H ₂ O | CO ₂ | CH ₄ | N ₂ | NaCl |
| Quartz I | | | | | | | | | | | | | | | | | | |
| PANVI-14-a2 | 1 | 1 | Lw-c | -8.0 | 10.9 | -60.8 | | | >230 | L | 85.6 | 14.0 | 0.5 | 92.0 | 5.4 | 0.5 | 0.0 | 2.1 |
| PANVI-14-a2 | 1 | 2 | Lw-c | -10.0 | 10.8 | | | | >240 | L | 68.0 | 13.9 | 18.1 | 89.7 | 6.5 | 0.9 | 1.1 | 1.8 |
| PANVI-14-a2 | 1 | 3 | Lw-c | -7.0 | 10.6 | -60.0 | | | >230 | L | 82.6 | 12.1 | 5.3 | 91.2 | 6.4 | 0.6 | 0.3 | 1.6 |
| PAN-III-8c5 | 2 | 4 | Lw-c | -5.1 | 7.2 | | | | | | 82.7 | 9.8 | 7.5 | 94.6 | 3.7 | 0.2 | 0.1 | 1.4 |
| PAN-III-8c5 | 2 | 6 | Lw-c | -4.8 | 7.1 | | | | 213.1 | L | 82.0 | 12.5 | 5.4 | 94.1 | 4.2 | 0.3 | 0.1 | 1.3 |
| PAN-III-8c5 | 2 | 7 | Lw-c | -5.6 | 6.0 | | | | 149.5 | L | 82.5 | 12.4 | 5.1 | 94.0 | 4.0 | 0.3 | 0.1 | 1.6 |
| PAN-III-8c5 | 2 | 12 | Lw-c | -9.4 | 9.2 | -58.1 | | | | | 72.8 | 8.2 | 19.0 | 88.3 | 8.3 | 0.7 | 1.6 | 1.1 |
| PAN-III-8c5 | 2 | 13 | Lw-c | -6.5 | 7.7 | -58.9 | | | | | 77.9 | 10.3 | 11.8 | 94.3 | 3.4 | 0.1 | 0.2 | 2.0 |
| PAN-III-8c6 | 2 | 16 | Lw-c | -6.1 | 6.9 | | | | 232.5 | L | 83.9 | 16.1 | 0 | 94.4 | 3.4 | 0.2 | 0.0 | 1.9 |
| PAN-III-8c5 | 2 | 18 | Lw-c | -5.6 | 6.2 | | | | | | 82.3 | 17.7 | 0 | 93.8 | 4.0 | 0.4 | 0.0 | 1.8 |
| PAN-III-8c5 | 2 | 5 | Lw-c | -7.8 | 8.7 | | | | 209.0 | L | 96.6 | 2.9 | 0.5 | 99 | 4.6 | 0.1 | 0.0 | 2.3 |
| PAN-III-8c5 | 2 | 15 | Lw-c | -4.6 | 8.8 | | | | | | 93.1 | 6.9 | 0 | 93.3 | 5.3 | 0.2 | 0.0 | 1.2 |
| PAN-III-8c5 | 2 | 9 | Lw-c | -5.7 | 10.1 | | | | 198.7 | L | 94.1 | 5.9 | 0 | 94 | 4.3 | 0.1 | 0.0 | 1.6 |
| PAN-III-8c5 | 2 | 8 | Lw-c | -4.7 | 10.1 | | | | 222.3 | L | 93.1 | 7.0 | 0 | 93.8 | 4.9 | 0.2 | 0.0 | 1.1 |
| Topaz II | | | | | | | | | | | | | | | | | | |
| PANXX-IA | IA | I.1.a | Lc-w | -5.0 | 9.6 | -58.7 | 19.2 | V | 260 | L | 91.2 | 2.7 | 6.1 | 91.6 | 6.5 | 0.1 | 0.3 | 1.5 |
| PANXX-IA | IA | II.1.a | Lc-w | -6.1 | 7.6 | -61.5 | 19.2 | V | 253 | L | 88.4 | 3.5 | 8.1 | 91.3 | 6.5 | 0.1 | 0.3 | 1.8 |
| PANXX-IA | IA | II.1.b | Lc-w | -6.1 | 7.1 | -61.7 | 18.9 | V | 256 | L | 86.5 | 4.1 | 9.4 | 91.4 | 5.3 | 0.1 | 0.3 | 2.9 |
| PANXX-IA | II | 4.a | Lc-w | -8.4 | 9.8 | -60.1 | 18.1 | V | 285 | L | 86.8 | 5.8 | 7.8 | 93.0 | 5.0 | 0.2 | 0.2 | 1.7 |
| PANXX-IA | IA | X.4 | Lc-w | -5.5 | 6.1 | -58.3 | 14.9 | V | 250 | L | 90.9 | 3.7 | 5.5 | 93.5 | 3.3 | 0.0 | 0.0 | 3.1 |
| PANXX-IA | III | 2.b | Lc-w | -5.2 | 8.1 | -58.9 | 18.9 | V | 250 | L | 88.9 | 3.2 | 7.9 | 90.4 | 6.5 | 0.1 | 0.4 | 2.6 |
| PANXX-IA | III | 2.d | Lc-w | -4.4 | 9.8 | -57.8 | 19.4 | V | 254 | L | 87.8 | 3.2 | 9.0 | 92.6 | 5.5 | 0.1 | 0.3 | 1.5 |
| PANXX-IA | IV/D | IV.1.a | Lc-w | -5.4 | 9.1 | -57.9 | 18.3 | V | 290 | L | 90.5 | 2.5 | 7.0 | 93.1 | 4.8 | 0.1 | 0.2 | 1.8 |
| PANXX-IA | III | 2.a.1 | Lc-w | -4.8 | 8.8 | -57.4 | 17.8 | V | 245 | L | 90.9 | 2.4 | 6.7 | 91.6 | 6 | 0.1 | 0.3 | 2 |
| PANXX-IA | IV/D | II.1.a | Lc-w | -4.7 | 9.3 | -58.0 | 19.2 | V | 250 | L | 90.4 | 3.1 | 6.5 | 91.3 | 6.5 | 0.1 | 0.3 | 1.8 |
| PANXX-IA | V | 2.b | Lc-w | -4.8 | 9.2 | -58.6 | 11.2 | V | 295 | L | 95.0 | 3.0 | 2.0 | 93.1 | 5.3 | 0.1 | 0.1 | 1.5 |
| PANXX-IA | V | 2.a | Lc-w | -5.2 | 8.6 | -59.3 | 10.6 | V | 285 | L | 87.0 | 4.1 | 8.9 | 93.8 | 3.5 | 0.2 | 0.3 | 2.3 |
| | | | | | | | | | | | | | | | | | | |
| PANXX-IA | IA | X.1 | Lw-c | -5.3 | 5.5 | | | | 248 | L | 83.3 | 5.3 | 11.4 | 94.8 | 3.3 | 0.1 | 0.2 | 1.6 |
| PANXX-IA | IA | X.3 | Lw-c | -5.6 | 5.9 | | | | 247 | L | 88.1 | 4.0 | 7.9 | 94.7 | 3.1 | 0.4 | 0.1 | 1.7 |
| PANXX-IA | II | 2.a | Lw-c | -6.9 | 8.0 | -61.7 | | | 254 | L | 81.8 | 9.2 | 9.0 | 93.2 | 4.3 | 0.2 | 0.3 | 2.0 |
| PANXX-IA | IV/D | III.1.a | Lw-c | -6.5 | 8.2 | | | | 255 | L | 85.6 | 6.4 | 8.0 | 94.1 | 3.7 | 0.1 | 0.1 | 2.0 |
| PANXX-IA | IA | X.2 | Lw-c | -5.5 | 5.8 | | | | 249 | L | 86.8 | 4.9 | 8.3 | 94.9 | 3.2 | 0.1 | 0.1 | 1.7 |
| PANXX-IA | IV/D | III.2.a | Lw-c | -5.7 | 8.4 | | | | 245 | L | 83.1 | 8.1 | 8.8 | 94.5 | 3.6 | 0.1 | 0.1 | 1.7 |
| PANXX-IA | IV/D | IV.3.a | Lw-c | -4.3 | 8.4 | -58.4 | | | 254 | L | 86.1 | 6.8 | 7.1 | 95.2 | 3.4 | 0.1 | 0.1 | 1.2 |
| PANXX-IA | I-A | I.1.b | Lw-c | -5.7 | 5.1 | -59.8 | | | 248 | L | 86.8 | 4.8 | 8.4 | 95.1 | 2.9 | 0.0 | 0.1 | 1.9 |
| | | | | | | | | | | | | | | | | | | |
| PANXX-IA | II | 1.a | Lc-(w) | -7.1 | 9.7 | -60.0 | 10.4 | L | 300 | L | 88.3 | 2.7 | 9.0 | 13.0 | 76.9 | 2.3 | 7.8 | 0.1 |
| PANXX-IA | II | 1.b | Lc-(w) | -5.1 | 9.7 | -59.9 | 10.3 | L | 299 | L | 87.1 | 2.7 | 10.2 | 13.0 | 75.8 | 2.3 | 8.8 | 0.1 |
| PANXX-IA | II | 1.c | Lc-(w) | -5.5 | 9.5 | -58.8 | 10.5 | L | 312 | L | 84.5 | 3.3 | 12.2 | 13.2 | 73.4 | 2.8 | 10.5 | 0.1 |
| PANXX-IA | II | 1.d | Lc-(w) | -5.2 | 9.7 | -58.7 | 11.6 | L | 304 | L | 84.6 | 3.5 | 11.9 | 13.4 | 73.3 | 3.0 | 10.3 | 0.0 |
| PANXX-IA | IV/D | IV.1.a | Lc-(w) | -4.9 | 9.8 | -59.4 | 11.3 | L | 295 | L | 85.2 | 3.2 | 11.6 | 24.3 | 64.6 | 2.5 | 8.5 | 0.0 |
| PANXX-IA | IV/D | IV.1.b | Lc-(w) | | 9.2 | -58.8 | 11.4 | L | 299 | L | 85.2 | 3.3 | 11.5 | 13.2 | 74.0 | 2.9 | 9.9 | 0.0 |
| PANXX-IA | IV/D | IV.1.c | Lc-(w) | | 8.6 | -58.7 | 12.5 | L | 289 | L | 83.3 | 3.7 | 13.0 | 13.3 | 72.2 | 3.2 | 11.2 | 0.1 |

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Table 2: Selected fluid inclusions with indications of microthermometric parameters, corresponding volatile phase composition from Raman spectroscopy, and calculated bulk compositions. L: homogenisation to the liquid phase, V: homogenisation to the vapour phase. See text for other abbreviations.