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► To cite this version:

Marion Turuani, Flavien Choulet, Aurélien Eglinger, Philippe Goncalves, Julie Machault, et al.. Geochemical fingerprints of brannerite (UTi₂O₆): an integrated study. *Mineralogical Magazine*, 2020, 84 (2), pp.313-334. 10.1180/mgm.2020.7. hal-03026641

HAL Id: hal-03026641

<https://hal.science/hal-03026641v1>

Submitted on 26 Nov 2020

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1 Geochemical fingerprints of brannerite (UTi₂O₆): an integrated study

2

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30

31 Abstract

32

33 Brannerite (UTi_2O_6) is among the major uranium-bearing minerals found in ore deposits,
34 but as it has been long considered as a refractory mineral for leaching, it is currently
35 disregarded in ore deposits. Brannerite is found in a variety of geological environments
36 including hydrothermal and pegmatitic, which represent the most frequent occurrences.
37 Based on scanning electron microscopy (SEM) observations coupled with electron probe
38 micro-analyzer (EPMA) and laser ablation inductively-coupled plasma mass
39 spectrometer (LA-ICPMS) analyses, this study describes the morphological features and
40 the chemical contents and trace element abundances of brannerite samples from five
41 hydrothermal and five pegmatitic localities across the world. Mineral chemistry is also
42 compared with transmission electron microscopy (TEM) observation and Raman
43 spectrometry, which show that brannerite is amorphous. Major results include the
44 definition of substitution trends and REE patterns, which are characteristics of either an
45 occurrence or a genetic type (hydrothermal and pegmatitic). Hence, combining the major
46 results, it is possible to obtain reliable constraints for establishing a geochemical
47 classification of brannerite. Inferred fingerprints have direct implications for forensic
48 science and the exploration industry; they also contribute to better understanding the
49 metallogenic processes and optimizing the extraction of uranium.

50

51 KEYWORDS: brannerite, fingerprints, hydrothermal, pegmatite, mineral chemistry

52

53 **Introduction**

54

55 Growing demand for energy requires a diversification of primary raw materials as
56 well as a re-evaluation of low grade ores, which may occur in large tonnage deposits.
57 Current primary ores processed in the nuclear industry mostly include uraninite (UO₂)
58 and coffinite U(SiO₄)_{1-x}(OH)_{4x}. Unconventional target ores include brannerite, a uranium
59 titanate (UTi₂O₆), because of its high U content of up to 55 wt% U (Patchett and Nuffield,
60 1960; Skymanski and Scott, 1982). Worldwide, brannerite is reported in a variety of
61 geological environments including sedimentary (*e.g.* Witwatersrand, South Africa; Smits,
62 1984), hydrothermal (*e.g.* Chateau-Lambert, France; Branche *et al.*, 1952), magmatic (*e.g.*
63 Crocker's Well, Australia; Ludwig and Cooper, 1984) and metamorphic (*e.g.* San
64 Bernardino county, USA; Hewett *et al.*, 1957) settings. In some deposits, brannerite is the
65 main U-bearing mineral, like at Elliot Lake, Canada (Szymanski and Scott, 1982), Mount
66 Isa, Australia (Wilde *et al.*, 2013) and Olympic Dam, Australia (Macmillan *et al.*, 2017). In
67 the Witswatersrand conglomerate, brannerite accounts for 8 to 19 wt% of the total
68 uranium mineralization (Lottering *et al.*, 2008). While U can be easily extracted from
69 oxide minerals, brannerite has long been considered as refractory to direct leaching and
70 for this reason it has not to date been extensively mined and/or processed (Vance *et al.*,
71 2000, and references therein). Recent advances in hydrometallurgy have shown that U
72 can be recovered from brannerite using acid solutions under physical- and chemical-
73 controlled conditions (Charalambous *et al.*, 2014). Uranium recovery from brannerite is
74 not a straightforward process and the efficiency of recovery is strongly influenced by the
75 ore paragenesis (Lottering *et al.*, 2008; Sapsford *et al.*, 2012). Although brannerite is

76 formed in a large variety of geological environments, its crystal chemistry and
77 petrogenesis remains under-investigated.

78 Brannerite crystallizes in the monoclinic system, with space group C2/m
79 (Szymanski and Scott, 1982). The general formula is best described to be AB₂O₆, where A
80 is U and B is Ti. Both A and B sites are distorted octahedra (six-coordinated), which share
81 corners and/or edges to form a structural framework (Szymanski and Scott, 1982, Fig. 1).
82 Natural brannerite is commonly non-stoichiometric, and exhibits variable compositions
83 related to more or less complex substitution mechanisms (Ditz *et al.*, 1990; Lumpkin *et*
84 *al.*, 2012; Macmillan *et al.*, 2017). The A site is mainly occupied by U, Ca, Th and rare earth
85 elements (REE), whereas the B site includes Ti, Al and Fe. Due to the high content of
86 radioactive elements (U, locally Th and their daughter elements), the self-irradiation of
87 natural brannerite causes significant structural damage leading to the amorphization of
88 the crystal lattice (Smith, 1984; Lumpkin *et al.*, 2012). Such processes lead to favourable
89 conditions for fluid circulation that contributes to the inception of alteration (Seydoux-
90 Guillaume *et al.*, 2015; Duran *et al.*, 2016) and further incorporation of impurities into the
91 brannerite structure. Such variations in composition, together with the complex nature of
92 brannerite ores have major effects on in dissolution rates of brannerite (Goldney *et al.*,
93 1972; Polito *et al.*, 2009; Charalambous *et al.*, 2012).

94 The detailed chemical characterization of minerals, like colombite-tantalite
95 (Melcher *et al.*, 2008) and uraninite (Mercadier *et al.*, 2011; Eglinger *et al.*, 2013; Frimmel
96 *et al.*, 2014) had led to classifications of minerals based on their geological environment.
97 Such chemical fingerprints have also direct applications to the exploration industry and
98 forensic science. Owing to the large variety of brannerite occurrences and its complex
99 crystal chemistry, a similar chemical characterization approach is developed in this
100 contribution. Based on both optical and electronic microscopy, major and trace element

101 analyses of natural brannerite minerals collected from magmatic (pegmatitic) and
102 hydrothermal occurrences, this study aims at identifying the chemical substitutions,
103 leading to a large variety of compositions. This characterization leads to a classification of
104 brannerite based on the genetic type of their occurrence. This enables us to discuss
105 implications for: (1) ore deposits fingerprints; (2) using brannerite as a dating tool; (3)
106 determining key parameters for optimized U recovery during leaching operations.

107

108

109 **Material and methods**

110

111 *Brannerite ores*

112 The studied samples include single crystals and ores collected from hydrothermal,
113 and pegmatitic occurrences worldwide (Fig. 2). In this section, only a brief geological
114 overview of the sampling localities is provided; more detailed information on ore deposits
115 or occurrences can be found in the appendix and in the referred literature. Five samples
116 from hydrothermal occurrences were studied: La Gardette (GD) from the French Western
117 Alps, Bou Azzer (BA) from the Moroccan Anti Atlas Belt, Chhuling Khola Valley (HL) in the
118 Nepalese Himalaya, Mont Chemin (MC) in the Western Swiss Alps, and Kratka Valley (KV)
119 in the Bohemian Massif. These hydrothermal veins formed after local or regional events,
120 without direct connection to a magmatic event, and they may record a complex evolution
121 of the fluid composition. Within veins, brannerite is spatially associated with gangue
122 minerals within a more or less polyphase paragenetic sequence.

123 Five samples from magmatic-pegmatitic occurrences were studied: Crocker's Well
124 (CW) in Central Australia, Hidden Valley (HV) in the Finders Ridge, Australia, El Cabril
125 (EC) in the Sierra Albararrana, Andalusia, Lodrino (BR1) in the South-Central Swiss Alps
126 and Marienfluss Valley (NA12) in Northern Namibia. These occurrences are generally
127 dykes spatially and/or temporally associated with magmatic and metamorphic
128 complexes. Pegmatite, which often corresponds to the last stage of the magmatic
129 evolution, is composed of K-feldspar, quartz, albite and, among accessory minerals (listed
130 in the appendix and in the referred literature), brannerite. For simplification, brannerite
131 formed in magmatic-pegmatitic environments will be named "pegmatitic brannerite",
132 while those formed in non-magmatic hydrothermal settings will be named "hydrothermal
133 brannerite".

134

135 *Analytical methods and data processing*

136

137 Polished thin-sections and plugs were prepared from rock samples and mineral
138 chips at GeoRessources, Nancy (France). Identification of the paragenesis and textures
139 was carried out using optical microscopy and scanning electron microscopy (SEM). SEM
140 instrumentation consists of FEI Quanta 450, equipped with an EDS spectrometer and a
141 backscatter electron detector (BSE), hosted by the MIMENTO platform (RENATECH
142 Network) at the Femto-ST lab, Besançon (France). We operated at acceleration voltages
143 between 10 and 15 kV.

144 As representative of pegmatite and hydrothermal settings, respectively, two thin
145 lamellae from Lodrino and Bou Azzer samples were prepared using a FEI Helios 600i
146 FIB/SEM instrument (MANUTECH USD, Saint-Etienne, France). After localization of the
147 area of interest by backscattered electron imaging, a first 300 nm-thick protective coating
148 of platinum was deposited. A thick amorphous carbon coating was then deposited using
149 a gallium ion beam. The TEM lamellae were firstly pre-thinned at 30 kV, transferred on a
150 Cu semi grid and thinned down to be sufficiently transparent to the electron beam (*i.e.*
151 less than 100 nm). The lamellae were finally cleaned at low voltage (down to 1 kV) in
152 order to remove defects created by the FIB process and to optimize its thickness.

153 Foils were cut within the apparently unaltered (homogenous domains with limited
154 grey-scale variations under the SEM in BSE mode) domains of brannerite grains from Bou
155 Azzer and Lodrino, considered as representative of hydrothermal and pegmatitic settings.
156 Foils observations were carried out at Centre Technologique des Microstructures (CT μ)
157 in Lyon 1 University (France), with a JEOL2100F transmission electron microscope (TEM)
158 operated at 200 KeV, equipped with an energy dispersive spectrometer (SDD Oxford) and

159 a High Angle Annular Dark Field (HAADF) detector used in Scanning Transmission
160 Electron Microscopy (STEM) mode.

161 Raman microspectroscopy was performed at ambient temperature on polished
162 thin-sections and plugs at IC2MP, Poitiers (France). Raman spectra were acquired using
163 a LabRAM HR800UV confocal microspectrometer (Horiba Jobin Yvon, Villeneuve d'Ascq,
164 France) equipped with a Peltier effect-cooled CCD (Charged Coupled Device) detector.
165 The excitation wavelength was set at 632.8 nm (He-Ne laser), or at 514.5 nm (Ar⁺ laser),
166 or at 532.4 nm (diode solid laser). Laser power delivered at the sample was *ca* 19 mW
167 (without filtering) and filters of optical densities of either 1 or 2 were used for all spectra.
168 Samples were analysed using a confocal high-stability BXFM Olympus microscope
169 equipped with either a 50 × LMPlan (numerical aperture: 0.55), or a 100× MPlan
170 (numerical aperture: 0.9) Olympus objective. The spatial resolution was *ca* 1 × 1 μm². The
171 spectrometer was calibrated with a pure silicon wafer using the Raman scattering line
172 centred on 520.7 cm⁻¹, which resulted in an accuracy of no less than 0.5 cm⁻¹. It consisted
173 in an 1800 grooves mm⁻¹ holographic grating. Spectra were recorded in the 50-1000 cm⁻¹
174 Raman shift range with a spectral bandwidth of either 3.2 cm⁻¹ (with a confocal hole
175 aperture of 200 μm at 532.4 nm), or of 8.4 cm⁻¹ (with a confocal hole aperture of 400 μm
176 at 514.5 nm). Data acquisition and processing were carried out using the LabSpec version
177 5 software (Horiba Jobin Yvon).

178 Major element composition of brannerite was obtained by electron probe micro-
179 analyzer (EPMA), at GeoRessources, Nancy (France), using a Cameca SX100 equipped
180 with five wavelength dispersion spectrometers (WDS). Carbon-coated polished thin
181 sections were analysed with an acceleration voltage of 20 kV, and a current of 100 nA. The
182 spatial resolution is *ca.* 1 μm, with an average acquisition time of 5 minutes. Oxides,
183 silicates, and pure metals were used as standards (Table A1). In addition, quantitative and

184 qualitative elemental composition maps were obtained using (1) a Field-Emission Gun
185 (FEG) Cameca SXFive FE, equipped with five WDS at Centre de MicroCaractérisation
186 Raimond Castaing at Toulouse (France) (for samples from Himalaya and El Cabril) and
187 (2) a JEOL 8200 Superprobe equipped with five WDS, hosted at University of Geneva (for
188 sample from Bou Azzer), respectively. In these cases, acceleration voltage was of 10 kV
189 and a current of 100 nA. Elemental composition maps were produced with a resolution of
190 1 μm and an acquisition time of 600 ms per pixel. Following Collela *et al.* (2005), U^{4+} , U^{5+}
191 or U^{6+} relative content was estimated on a basis of 6 oxygen atoms and 3 cations. There is
192 no unique solution to balance charges, therefore the average valence state has been
193 chosen as the most reliable parameter.

194 The minor and trace element contents were quantified using a laser ablation (193-
195 nm excimer Geolas Q Plus System) coupled to an inductively-coupled plasma mass
196 Spectrometer (Agilent 7500c Quadrupole) at Georessources, Nancy (France). The fluence
197 was 5 J cm^{-2} , using a repetition rate of 5 Hz. The laser spot sizes were 24 or 32 μm in
198 diameter, depending on the size of brannerite crystals. The total acquisition time,
199 including background and signal was limited to 200 s per analysis, with a background
200 acquisition of 30 s before ablating the material for 40 s. The following elements were
201 measured: B, Mb, Al, Si, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, the REEs, Pb, Th, U with
202 a dwell time of 10 ms (except 5 ms for U and Pb). The cycle time was 394 ms. The He flux
203 was fixed at 0.5 l.min^{-1} and 0.9 l.min^{-1} of Ar was added before entering the plasma. The
204 reference material was a SRM NIST 610 glass standard (Pearce *et al.*, 1997) and Ti and/or
205 U contents measured by EPMA on the same area were used as an internal standard. Data
206 reduction was carried out with IOLITE software (Paton *et al.*, 2011). Analytical precision
207 is calculated for all elements analyzed using standard deviation of recorded intensity and
208 is better than $\pm 15\%$ for concentrations higher than 10 ppm and becomes greater ($\pm 50\%$

209 to $\pm 70\%$) for concentration lower than 10 ppm. Limit of detection varies for each element
210 as a function of signal intensity and was calculated for each ablation from signal
211 intensities using the 3σ criterion (Longerich *et al.*, 1996). The most commonly achieved
212 LODs are below 2 ppm for the measured trace elements.

213 The comparison between chemical compositions of brannerite from different
214 deposits was achieved by estimating the difference in content of a given element (see
215 detailed procedure in Machault *et al.*, 2014). For this, we first calculated the coefficient of
216 variation defined by $Cv (\%) = \sigma/\mu$ (where σ is the standard deviation and μ is the average)
217 to describe the degree of homogeneity for the distribution of the analysed elements. The
218 non-parametric Kolmogorov–Smirnov test (*e.g.* Press *et al.*, 1986) was then used to
219 compare two populations and therefore evaluate the homogeneity between two samples.
220 We also applied multivariate statistical processing, to highlight the substitution trends
221 within brannerite. The principal component analysis (PCA) is a powerful variable-
222 reduction technique, which is more and more applied to geochemical data (*e.g.* Belissant
223 *et al.*, 2014). By recalculating principal components, which are defined as orthogonal
224 linear combinations of the initial variables, it is possible to project multivariate data in
225 two-dimensions with minimal data loss. The two first principal components, which are
226 used in this study, carry the highest explained variance, corresponding to the most
227 significant relationships between the variables. More detailed about PCA method can be
228 found in Koch (2012). For all calculations, we used R software and FactorMin R package
229 for PCA (Lê *et al.*, 2008).

230

231 **Results**

232

233 *Petrography of brannerite ores*

234

235 *Hydrothermal brannerite*

236

237 Brannerite crystals from La Gardette occur as laths, associated with Bi-Cu minerals
238 (emphlectite and wittichenite), native gold and quartz (Fig. 3a). A corroded boundary is
239 always observed and composed of newly formed and chemically different brannerite,
240 cerussite, REE phosphates, and iron oxides. Brannerite include minute inclusions of U-
241 rich minerals (not determined), while inclusion-free brannerite veins are also very
242 common in the studied crystals.

243 Samples from Bou Azzer exhibit elongated laths of brannerite associated with
244 quartz, barite and minor galena (Fig. 3b). Except for the presence of galena inclusions, BSE
245 images of brannerite crystals show a rather homogeneous internal structure suggesting
246 that brannerite crystals may be chemically homogeneous. However, element distribution
247 mapping reveals a complex inner structure within crystals (Fig. 4a-d), marked by the
248 presence of sub-rounded domains with varying Fe contents (Fig. 4d) Alteration also
249 occurs as partial to full replacement (Fig. 3b), marked by an intricate association of U-rich
250 and U-poor Ti oxides that coexist with coffinite and sulphate minerals (barite, anglesite)
251 (Fig. 3c).

252 Millimetre-sized anhedral crystals of brannerite from Himalaya are enclosed in
253 albite. BSE images and X-ray mapping reveal at least three distinct stages of brannerite
254 crystallization (Figs. 3d, 4e-h). The first stage (Br I) is characterized by oscillatory-zoning
255 and U, Th and Y chemical variation (Fig. 4f-h). This primary brannerite is cross-cut by two
256 successive generations of veins (Br II and Br III) that may resemble stockwerk. These
257 veins are rich in U and poor in Y and Th. Alteration rims are very limited, but a Cu-U-

258 bearing arsenate, possibly (meta-) zeunerite, and unidentified phosphate minerals are
259 commonly found around these crystals.

260 Brannerite from Mont Chemin occurs as small crystals (less than 150 μm),
261 associated with anatase, biotite, K-feldspar, REE carbonates and minor uraninite
262 inclusions. Crystals are usually prismatic and display a large rim of altered brannerite
263 (Fig. 3e). At Kratka Valley, brannerite occurs as sub-rounded crystals within a quartz
264 matrix. Fractures are frequent and numerous inclusions of Ti oxides and uraninite are
265 observed (Fig. 3f). Alteration is pervasive.

266 In the sample from Bou Azzer, TEM-Bright Field (BF, Fig. 5a) and STEM-HAADF
267 (High Angle Annular Dark Field) (STEM-DF, Fig. 5b) images reveal the presence of a dense
268 network of inclusions, either enriched in U (Fig. 5c) or in Pb (Fig. 5e). Selected Area
269 Electron Diffraction (SAED) patterns identified within brannerite and dark U-rich
270 inclusions result in broad diffuse rings equivalent to amorphous material (inset in Fig.
271 5a). The only trace of nano-crystalline material within the Bou Azzer sample corresponds
272 to the cubic-like Pb-rich inclusion, certainly galena. The amorphous state of natural
273 hydrothermal brannerites is also evidenced by Raman microspectroscopy (Fig. A1). The
274 Raman spectra of hydrothermal brannerite samples, acquired in unaltered domains (Fig.
275 3), do not exhibit the characteristic features of pure synthetic brannerite (Mesbah *et al.*
276 2019). The Raman spectra of brannerite samples exhibit a small but significant feature at
277 151 cm^{-1} (only for La Gardette sample) and broad and poorly resolved features around
278 600, 750, and 820 cm^{-1} (Fig. A1).

279

280 *Pegmatitic brannerite*

281

282 Samples from Crocker's Well display sub-rounded elongated crystals of brannerite
283 that displays intensive microfracturation (Fig. 6a). Brannerite is associated with Ti oxides,
284 which are also present as micrometre-sized euhedral inclusions within brannerite. Along
285 fractures and in the rim, U-Th rich silicates (possibly uranothorite) coexist with
286 brannerite, although no genetic relationships can be demonstrated. This association is
287 characteristic of an altered zone, which may also display U-depleted zones (Fig. 6a) and
288 apatite. Microfractures are filled with U-Th secondary products, which are too small to be
289 identified with the techniques employed here.

290 Brannerite from Hidden Valley is a single elongated millimetre-sized crystal, which
291 displays well-developed corroded boundaries and transversal fracturing with alteration
292 (Fig. 6b). Preserved brannerite exhibits tiny uraninite inclusions. The rim is zoned,
293 showing differences in U depletion; it also contains secondary U-Th minerals, which
294 belong to the thorite-coffinite series, according to Raman spectroscopic analyses.

295 The studied single crystal of brannerite from El Cabril is also characterized by a
296 pervasive corroded boundary (Fig. 6c), but we also observed the presence of parallel
297 fractures filled with a symplectite-like association of uraninite, Ti-oxides and an unknown
298 yttrium-rich phase (Figs. 6d, 7a-d). At sites of dilational jogs, uraninite crystals are bigger
299 in size, but still anhedral. This fracturation/filling stage predates alteration, which occurs
300 as a large and complex rim, surrounding the single crystal. This rim presents a succession
301 of U-depleted domains with locally botryoidal aggregates and thin lamina of U-Ti oxides.

302 Euhedral prismatic brannerite crystals from Lodrino are associated with K-
303 feldspar. They do not display any evidence of internal texture, but, locally, a complex
304 zoned rim of altered brannerite has been observed (Fig. 6e). Brannerite from Namibia is
305 also a single crystal, which presents a sub-rounded irregular shape. Inclusions are rare
306 within brannerite, but fractures are locally filled with uraninite partially replaced by

307 coffinite (Fig. 6f). Interestingly, brannerite can also occur with a colloidal texture, very
308 similar to frequently observed pitchblende (Fig. 6f).

309 In the Lodrino sample, BF-TEM and DF-STEM images show the presence of altered
310 domains within brannerite (Fig. 8a-b), with a variation in composition for U, Ti, and Si (Fig.
311 8c-e). The brightest parts within this area (Fig. 8b) seem to be enriched in Si sometimes
312 correlated with U enrichment. In contrast, darker areas are depleted in U and Ti. Pristine
313 brannerite areas only reveal U and Ti. The diffraction pattern within the unaltered
314 brannerite domain indicated it is completely amorphous (inset in Fig. 8a above); in
315 contrast the diffraction pattern from the altered domain shows evidence of nano-
316 crystalline material, with two intense rings with d-spacings of 3.45 Å and 1.87 Å (inset at
317 the bottom in Fig. 8a). The amorphous state of natural pegmatite brannerites is confirmed
318 by Raman microspectroscopy (Fig. A1), since like for hydrothermal brannerite, the Raman
319 spectra acquired in unaltered domains (Fig. 6), do not exhibit the characteristic features
320 of pure synthetic brannerite (Mesbah *et al.* 2019). Again, with the exception of the well-
321 defined feature at 151 cm⁻¹ for the sample from Namibia, only broad and poorly resolved
322 features around 600, 750, and 820 cm⁻¹ (Fig. A1).

323

324 *Major and minor element content*

325

326 The composition of brannerite was obtained from domains that appear
327 homogenous and middle grey under the SEM (Figs 3, 6), away from corroded grain
328 boundaries (*e.g.* Figs. 3a, 6c) and altered domains *e.g.* along fractures (*e.g.* Figs. 6b, 6f).
329 Table 1 and boxplots of Fig. 9 summarize the distribution of major and minor element
330 contents, expressed in atom per formula unit (apfu), following Collella *et al.* (2005; see
331 section "Materials and Methods"). The measured U content is always less than 1 atom per

332 formula unit. While Ti content of hydrothermal brannerite ranges from 1.9 to 2.1 apfu,
333 this value is always less than 2 apfu for pegmatitic brannerite, except for BR1.

334 For major and minor elements, we observe variations in chemical composition
335 between geological settings. For instance, aluminium in hydrothermal brannerite is
336 always lower than 0.01 apfu, while brannerite from pegmatites have wider range in Al
337 contents. Chemical variations are also observed within a single geological environment.
338 Ti, Fe and Y for hydrothermal brannerite show significant variations, while U, Ca and Th
339 are the most variable components in pegmatitic brannerite. Finally, significant chemical
340 variations are also observed for a given occurrence: *e.g.* U, Y, and Th for Himalaya and Ti,
341 Fe and Si for Bou Azzer. Such variability of element content within a single sample is also
342 revealed by element chemical maps, which display chemical zoning within crystals (*e.g.*
343 U, Th and Y in brannerite from Himalaya, Fig 4e-h).

344

345 *Trace element content*

346

347 The trace element content may vary by several orders of magnitude depending on
348 samples, sample locality and sample type (Table 2, Fig. 10). Trace element concentration
349 may reflect the local geological environment, like the high chromium content in Bou Azzer
350 that is related to the occurrence of metasomatized ophiolites hosting the deposit (Fig.
351 10a). In the case of Mn and Nb, no clear signature can be pointed out at the scale of deposit
352 type (Fig. 10b-c), although the Mont Chemin sample shows high concentrations in these
353 two elements. For metals like Cu and Zn (Fig. 10d-e), no clear trend can be observed,
354 except local enrichment in Cu and Zn for brannerite from Mont Chemin. The Pb content
355 distribution between samples is very heterogeneous (Fig. 10f): this may either reflect
356 local Pb enrichment as it correlates with high Zn and Cu contents (*e.g.* Mont Chemin),

357 and/or enrichment due to production of radiogenic lead (as a result of elapsed time since
358 crystallization). In this latter case, old and high U+Th brannerite like Crocker's Well and
359 Hidden Valley have a Pb content that displays orders of magnitude higher than the
360 youngest brannerite from Lodrino.

361

362 *Principal component analysis major and minor elements*

363

364 The results of the PCA applied to the EPMA dataset are displayed in Figure 8, where
365 spot analyses (individuals, to the left) and elements (variables, to the right) are projected
366 on the PC1 vs. PC2 plane. For the hydrothermal brannerite dataset, loadings of PC1 and
367 PC2 represent 49.85% of the element content variability (Fig. 11a-b). The PCA plot
368 underlines two main opposed pairs of element clusters. For the first pair mostly loaded
369 by PC1, one group is composed of Ce, P, Y, and Nd, while the other group includes U and
370 Th. For the second pair mostly loaded by PC2, a cluster composed of Fe, Mg, Ca and Si is
371 opposed to Ti. Spot representation in the PC1 vs. PC2 plane refers to the sample location.
372 PC1 (mostly loaded by U, Th, and REE) is correlated with samples from Mont Chemin and
373 Himalaya, whereas PC2 (loaded by Ti, Ca, Fe) is correlated with samples from Bou Azzer,
374 Kratka Valley and La Gardette.

375 For pegmatite samples, PC1 and PC2 represent 56% of chemical composition
376 variations (Fig. 11c-d). The PCA also reveals some differences like Si and Th that are now
377 observed as clusters in association with REE and P. The group of elements opposed to Ti
378 includes Al, but not Ca, which occupies an intermediate position. All individuals are
379 grouped, without any overlap of sample localities (Fig. 11c). As a result, two subgroups
380 can be distinguished. While a first one (PC1 loading) including the Crocker's Well, Hidden

381 Valley, and El Cabril samples correlates with U, Th and REE, a second one (PC2 loading)
382 composed of Namibia and Lodrino samples, correlates with Ti, Al and Fe.

383

384 **Inferred chemical substitutions in brannerite**

385

386 The EPMA analytical totals, expressed as weighted per cent of oxides (wt%) for
387 each analysis range between 95% and 100%, except for samples from Bou Azzer (mean
388 92.11 wt%) and Crocker's Well (mean 92.61 wt%) samples (Table 1). This range is
389 consistent with values provided by Charalambous (2013) and Macmillan *et al.* (2017).

390 Totals lower than 100% can be related to several factors:

391 (1) Among REEs, only Ce and Nd were measured by EPMA, and both elements account for
392 only 15 to 50% of the total REE of the sample, depending on the LREE anomaly (see
393 section *Trace elements variation*);

394 (2) We assumed that EPMA-measured oxygen only occurs as O²⁻ anions within the
395 brannerite structure. However, U (and Th) α -decays induce radiation damage leading to
396 amorphization of the brannerite crystals as confirmed by TEM imaging (Figs. 5, 8) and the
397 complete loss of the Raman vibrational mode (Fig. A1). The self-radiation damages
398 (metamictization), which affect the crystal structure of brannerite can contribute to
399 incorporation of either H₂O or OH⁻ (Lumpkin *et al.*, 2012). These authors reported H₂O
400 contents between 0 and 3.7 wt%, and up to 7.4 wt% in highly damaged crystals from
401 Crocker's Well. Other deviations from ideal stoichiometry (AB₂O₆) can be achieved
402 through vacancies or excess oxygen (Colella *et al.*, 2005);

403 (3) Calculations of weighted oxide content assumed a unique valence for U (U⁴⁺), Fe (Fe³⁺),
404 Ce (Ce³⁺) and Pb (Pb²⁺). While this is probably correct for the three latter ones, direct
405 measurements of uranium chemical states on brannerite samples have demonstrated that

406 higher valence states (5+ and 6+) should be considered (Vance *et al.*, 2000, 2001; Finnie
407 *et al.*, 2003).

408 Our dataset confirms the variability of brannerite compositions reported in the
409 literature (Lumpkin *et al.*, 2012; Macmillan *et al.*, 2017), but in these studies, no
410 distinctions were made based on the geological environment where brannerite
411 crystallized. As shown by the respective locations of variable (elements) and individuals
412 (samples) clusters in the PCA plots (Fig. 11), chemical heterogeneity is mostly due to
413 replacement of Ti by Fe, Al and U by other cations, like Th, Ca, REE and Y with similar ionic
414 radius in 6-fold coordination sites (Shannon, 1976).

415 Uranium substitutions in the A site by Th, Ca, REE and Y account for up to 50% of
416 A site occupancy (Table 1). Substitution between U and Th is straightforward:



418 But this substitution is important only in brannerites from Mont Chemin, Hidden Valley
419 and Crocker's Well (Fig. 12a-b). For other cations (Ca, REE, Y), coupled substitutions must
420 be considered to account for their incorporation (Lumpkin *et al.*, 2012). The Ca content in
421 the A site is always associated with higher calculated average U valences (Fig. 12c), which
422 may reflect the following substitutions.



425 While the presence of U⁶⁺ is commonly observed in U minerals formed under oxidizing
426 conditions, the presence of U⁵⁺ was presumed in the Ca-rich brannerite from El Cbril
427 (Vance *et al.*, 2001). René and Dolníček (2017) also proposed these substitutions to
428 explain the high Ca content of brannerite from the Bohemian Massif.

429 PCA analysis shows an excellent correlation between P and Y + REE (Fig. 11)
430 suggesting that phosphorus could also be involved in the substitution of U⁴⁺ in the A site
431 via the substitution:



433 Although the ionic radius of P⁵⁺ (0.38 Å) is very different from that of U⁴⁺ (0.89 Å), the
434 partial destruction of the crystal structure of brannerite through metamictization may
435 have favoured the incorporation of P into the octahedral coordination A site (Shannon,
436 1976). In our case, the REE + Y contents (up to 5 x 10⁴ ppm) cannot be counterbalanced
437 via substitution (4), because of low average P contents (10² ppm). The incorporation of
438 REE and Y in the A site is also made possible by substituting and oxidizing U⁴⁺ into U⁵⁺
439 through substitution



441 Fig. 12c-f shows that hydrothermal brannerite from La Gardette and Himalaya are
442 characterized by a clear relationship between Y + Ce and U⁴⁺ or average U valence
443 consistent with the substitution vector of equation (5). Brannerites from pegmatites also
444 show a correlation between U⁴⁺ and Y + Ce apfu, but with a different slope. This difference
445 can be due to either unanalysed REE (and fractionation between the REE) or a different
446 substitution mechanism. This relationship between Y + REE substitution in the A site and
447 the genetic type has also been reported in Olympic Dam brannerite, which belongs to
448 different generations (Macmillan *et al.*, 2017).

449 Composition variability of brannerite is also due to replacement of Ti by different
450 cations up to a maximum of 25% of the B site occupancy. PCA analysis of Fig. 11 shows
451 that Ti and Fe³⁺ +/- Al³⁺ are correlated in both hydrothermal and pegmatitic brannerite.
452 In the pegmatitic brannerite, substitution of Ti by these tetravalent cations induces a

453 charge deficit on the B site that could be compensated by higher valences of U on the A
454 site, through coupled substitutions like



457 Fig. 10 shows a correlation between Ti or U average valence with $\text{Fe}^{3+} + \text{Al}^{3+}$, which is
458 consistent with substitutions (6) and (7). The respective contribution of substitutions (2),
459 (3), (5), (6) and (7) in the A and B sites to the average valence is difficult to ascertain,
460 except for pegmatitic brannerite from Namibia (Fig. 13). In this case, the limited amount
461 of Ca, REE and Y (<0.1 apfu) (Fig. 12) cannot account for the high average valence (4.63)
462 of U that is better explained by high Fe and Al content (0.25 to 0.4 apfu; Fig. 13). Coupled
463 substitutions involving Ti or other cations of the B site, as proposed in Lumpkin *et al.*
464 (2012) and Macmillan *et al.* (2017) could also explain the absence of direct correlation
465 between U and Ca in the PCA plots for hydrothermal and pegmatitic brannerite (Fig. 11).

466 Lumpkin *et al.* (2012) proposed an alternative substitution to compensate the
467 charge deficit induced by the replacement of Ti by Fe and Al:



469 In our case, there is no positive correlation between Fe, Al, and Nb. Fe-Al-poor
470 hydrothermal brannerite is rich in Nb, whereas pegmatitic brannerite generally presents
471 higher Al and Fe contents and is depleted in Nb (Figs 9c-d, 10c). MacMillan *et al.* (2017)
472 also suggests that missing charges could be due to the removal of OH^- anions through the
473 substitution $\text{Ti}^{4+} + \text{OH}^- = (\text{Fe}^{3+}, \text{Al}^{3+})$ (9), since appreciable water contents up to 7.4 wt%
474 have been measured in natural brannerite (Lumpkin *et al.*, 2012).

475 For hydrothermal brannerite, substitutions on the B site are limited and in many
476 cases the calculated Ti amount exceeds 2 apfu (Fig. 13a). Such deviation was also reported
477 in magmato-hydrothermal brannerites from Olympic Dam (Macmillan *et al.*, 2017) and

478 different hypotheses can be advanced: (1) coupled substitutions across the two sites; (2)
479 nanometric inclusions of Ti oxides intergrown with brannerite, similar to macroscopic
480 structures in magmatic and metamorphic brannerite (Figs 2, 4); (3) vacancies or other
481 substituents at the anion sites, causing overestimation of the cation content in the
482 structural formula calculation; (4) alteration processes leading to a partial removal of U,
483 without changing the crystal texture at the microscale. The Raman spectra obtained from
484 La Gardette and Namibia brannerites show a very small and broad band at around 640
485 cm^{-1} and the characteristic E_g mode at 151 cm^{-1} (Fig. A1). Such features are interpreted as
486 a spectroscopic signature of nanocrystalline anatase, probably blue-shifted with regard
487 to the corresponding mode of its core crystalline counterpart, displaying a significant
488 broadening of its profile (Bonne *et al.* 2010). This is the result of the metamictization of
489 brannerite crystals, even in the unaltered domains.

490 As noted by Lumpkin *et al.* (2012) and Macmillan *et al.* (2017), there is almost no
491 correlation between Ti and Si abundances, as occupancy of octahedral sites by Si is
492 impossible in low-pressure oxide compounds (Mysen and Richet, 2005). PCA plots display
493 very heterogeneous trends for Si relative to other elements (Fig. 11). While, for
494 hydrothermal brannerite, we may note a correlation between Si and Ti, for pegmatitic
495 samples we rather observe Si opposed to U along the PC1 (Fig. 11). This suggests either
496 an addition of Si within A sites, or the presence of nanoscale U-bearing silicates such as
497 coffinite. TEM-EDS chemical mapping revealed that parts of brannerite altered domains
498 are enriched in Si and depleted in U (Fig. 8a-e).). From the SAED patterns taken in this
499 altered domain (Fig. 8a), apart from diffuse rings corresponding to amorphous material,
500 additional diffraction spots with equivalent d-spacings of 3.45 Å and 1.87 Å could
501 correspond to the (200) and (321) planes of coffinite (3.41 Å and 1.88 Å, respectively from
502 Pointeau *et al.*, 2009), although those of brannerite (3.50 Å and 1.85 Å) are very close. For

503 comparison, in (Y, REE, U, Th)-(Nb-Ta-Ti) oxide minerals, altered domains were also
504 characterized by Si gain and U loss. This alteration results from fluid-mineral interaction,
505 favoured by fracturing due to radiation damage accumulated in U and Th-rich oxide
506 minerals (Duran *et al.*, 2016). A very similar process probably occurs for brannerite as (1)
507 all crystals of natural brannerite are metamict (Figs. 5, 8, A1) and (2) Si-rich brannerite
508 (*e.g.* Crocker's Well and Hidden Valley) are characterized by radial fracturing and well-
509 developed altered domains (Fig. 6a-b). Further careful nanometric observations and
510 additional brannerite synthesis in Si-rich environments are necessary to better
511 understand the mechanisms for Si incorporation within brannerite.

512

513 **Brannerite fingerprints**

514

515 *Major element and substitution*

516

517 These new results show that each locality and each genetic type are characterized
518 by various types and degrees of substitution, either on the A or on the B sites (Fig. 14).
519 Fig. 14a shows that hydrothermal brannerite is mostly characterized by a predominance
520 of A site substitution (90%), while pegmatitic brannerite generally presents a higher
521 proportion (20%) of B site substitution. Pegmatitic brannerite from Namibia represents
522 an extreme case, with a predominance of B site substitution (70 to 90%). The
523 incorporation of Si, whose mechanism is not well understood, seems to increase when
524 both A and B site substitutions are present (Fig. 14a). However, this could also reflect the
525 degree of alteration and mirrors the possible modification of the initial chemical
526 composition of brannerite.

527 Brannerite populations can also be distinguished based on the cations
528 incorporated in sites A and B via the substitutions described previously. In hydrothermal
529 brannerite, except for Th-rich brannerite from Mont Chemin, A site substitution is mostly
530 characterized by high REE + Y contents, with local enrichment in Ca such as in Bou Azzer
531 (Fig. 14b). For pegmatitic brannerite, A site is characterized by (1) an equal distribution
532 of Th and Y + Ce and (2) various degree of Ca substitution (Fig. 14b). In uraninite formed
533 under hydrothermal conditions, the Th content is usually negligible as Th is less mobile
534 and Th⁴⁺ displays very low solubility (Cuney and Friedrich, 1987). In magmatic
535 environments, the Th content generally increases (*e.g.* Förster, 1999; Frimmel *et al.*,
536 2014), except if the source of radiogenic elements (magma or protolith) is initially poor
537 in Th. In the B site, while only Fe³⁺ replaces Ti in hydrothermal brannerite, pegmatite
538 brannerite are characterized by the incorporation of both Fe³⁺ and Al, with an Al/Fe³⁺
539 ratio around 1:6 (Fig. 14c).

540 Strong variations in chemical composition are also observed at the scale of a given
541 sample or locality, as exemplified by the case of Himalaya. Although morphological
542 differences support the presence of three brannerite generations (Fig. 4e-h), their
543 composition follows the same substitution trends (1) and (5). This suggests dissolution -
544 reprecipitation process of brannerite without an external chemical contribution. This
545 observation differs from the results reported at Olympic Dam, in which four generations
546 of brannerite are related to distinct substitution mechanisms (Macmillan *et al.*, 2017).

547 In addition to substitution-related fingerprints (Fig. 14), it is possible to obtain
548 individual signatures for either the brannerite genetic type or the brannerite locality
549 using statistical methods. The non-parametric Kolmogorov–Smirnov test was used to
550 compare the distribution of two populations and therefore evaluate the homogeneity
551 between two samples for a given element. The statistical analysis shows that element

552 content distributions significantly differ (at 95%) between samples, suggesting that each
553 locality has its own mineral chemistry (Fig. 15). However several samples show a weaker
554 range of differing elements, supporting that these localities are close in terms of mineral
555 chemistry (*e.g.* BA and KV or CW and HV). This is an agreement with the distribution
556 observed in PCA (Fig. 11) and classification plots (Fig. 14).

557

558 *Trace elements variation*

559

560 Fingerprints can also be deduced from trace elements measured in brannerite. As
561 mentioned in section 3.3, interpreting the trace element content (Fig. 10) is difficult as
562 some elements may either (1) be or not be associated with coupled substitution (*e.g.* Nb);
563 (2) reflect the local geological environment (Cr at Bou Azzer); (3) derive from different
564 sources (*e.g.* common versus radiogenic Pb). In the case of REE, their incorporation is
565 associated with stoichiometric rules, as ionic radii of REE are close to U, despite a relative
566 lack of knowledge of charge balance mechanisms. The shapes of REE patterns differ
567 between the two genetic types:

568 (1) Hydrothermal brannerites are marked by a bell-shape (Fig. 16a). MREE such as Tb
569 (0.92 Å), Dy (0.91 Å), Ho (0.90 Å) and Er (0.89 Å) have ionic radii very close to that of U⁴⁺
570 (0.89 Å) in 6-fold coordination (Shannon, 1976) and, therefore, are most easily
571 incorporated in the brannerite structure. Similar patterns were observed for uraninites
572 formed in unconformity deposits (Pagel *et al.*, 1987; Mercadier *et al.*, 2011; Frimmel *et al.*,
573 2014). The total amount of REE is usually high (more than 10000 ppm) and the
574 LREE/HREE ratio oscillates between 0.3 and 3.8 (Fig. 17).

575 (2) At high temperature (>500°C), the brannerite structure dilates (Zhang *et al.*, 2006)
576 allowing the incorporation of REE, without any fractionation due to differences in ionic

577 radii. Pegmatitic brannerites are marked by LREE depletion, or a regular decrease from
578 HREE towards LREE (Fig. 16b). The total amount of REE shows strong variations (Fig. 17),
579 probably due to competitive substitutions at site A (Fig. 14c). In addition to a general
580 fractionation between LREE and HREE, it is worth noting that the fractionation rate
581 (LREE/HREE) increases with the total amount of REE (Fig. 17).

582 For the same sample type or locality, the REE patterns are very consistent (Fig. 16).
583 Minor differences may be mostly due to variations of total REE and/or a change in the
584 europium anomaly. In most cases, the Eu anomaly is absent or slightly negative attesting
585 for an early fractionation of Eu by feldspars, which are described in almost all mineral
586 associations. Eu positive anomalies are reported in La Gardette and El Cabril and could be
587 associated to a local change of redox conditions. It is noteworthy that positive anomalies
588 in El Cabril samples tend to be associated with the high total REE analysis (Fig. 16b).
589 Cerium also shows a frequent positive anomaly, which is also related to redox conditions
590 (*e.g.* Mont Chemin). Under oxidizing conditions, Ce^{3+} changes to Ce^{4+} , which is
591 preferentially incorporated in site A of brannerite, since its ionic radius (0.87 Å for Ce^{4+}
592 in 6-fold coordination; Shannon, 1976) is close to that of U^{4+} (0.89 Å) and its addition does
593 not require charge balance.

594 These results suggest, that beyond crystal-scale controls, addition of REE also
595 depends on external parameters such as temperature, but also of the presence of other
596 mineral phases that may trigger REE fractionation (Fig. 16c). Among them, monazite,
597 which was reported in several brannerite-bearing samples, preferentially partition LREE
598 and could be at the origin of the LREE-depleted patterns of most of brannerite.

599

600 **Implication of brannerite systematics**

601

602 *Fingerprints for tracking origin of ore*

603

604 Defining brannerite fingerprints offers a potential useful application in tracking
605 down the source of possibly illegally mined uranium ores. Such an approach was applied
606 to a variety of conflict or strategic minerals, like colombo-tantalite (Melcher *et al.*, 2008,
607 2015), gems (Giuliani *et al.*, 1998, 2005) and uraninite (Mercadier *et al.*, 2011; Frimmel *et*
608 *al.*, 2014; Spano *et al.*, 2017). Chemical fingerprints of brannerite consists of a combined
609 characterization of the major substitution trends (A and B sites), the nature of elements
610 incorporated, and the shape of REE patterns. Other trace elements can be used as they
611 may represent a locality-specific feature, which may be useful in forensic studies.
612 However, as shown by this study and reported in previous literature (*e.g.* Charalambous
613 *et al.*, 2012; Lumpkin *et al.*, 2012; Macmillan *et al.*, 2017), brannerite ores are generally
614 complex and include other uranium minerals (*e.g.* uraninite, coffinite) and/or successive
615 generations of brannerite with variable mineral chemistry (Fig. 4e-h). Hence, traceability
616 studies cannot be done at ore scale, but require careful consideration of U-bearing mineral
617 phases. A complementary signature using isotope systematics (O, U, Th, Pb) as proposed
618 for uraninite (*e.g.* Pajo *et al.*, 2001) could also be a useful tool to provide unequivocal
619 source for brannerite.

620

621 *Using brannerite as a tool for dating mineralizing events*

622

623 The high U (and Th) abundance makes brannerite a good candidate tool for dating
624 mineralizing events. Previous geochronology was carried out using a variety of
625 techniques including the ID-TIMS (Ludwig and Cooper, 1984; Copeland *et al.*, 1991) and
626 the LA-ICPMS (Oberthür *et al.*, 2009) over a large range of ages (4.8 Ma to 670 Ma). These

627 published geochronological data lack in most cases detailed petrography to support
628 unequivocal evidence for (1) unique brannerite chemistry close to ideal composition to
629 limit matrix effects and (2) single crystallization stage to avoid mixing between different
630 age populations. The nature of Pb is another crucial issue that needs to be considered for
631 dating application. In 6-fold coordination, the respective ionic radii of Pb^{4+} and Pb^{2+} are
632 0.77 Å and 1.19 Å, respectively (Shannon, 1976), suggesting that Pb poorly substitutes for
633 U at the A site. The dilatation of the crystal structure at high temperature probably enables
634 a larger addition of Pb^{2+} in brannerite, but this cannot explain the local Pb enrichment
635 (*e.g.* more than 10000 ppm at Montchemin; Fig. 10f). Radiogenic Pb produced by decay of
636 U and Th, can be present in significant concentration in old brannerite, like Hidden Valley
637 and Crocker's Well (Fig. 10f). Significant lead loss has also been reported, which makes
638 geochronological data interpretation even more challenging (Lumpkin *et al.*, 2012).
639 Furthermore, the common association of brannerite with galena at various scales (Figs. 3,
640 5, 6) also questions the origin of the measured Pb. Lead is a network modifier and thus,
641 as brannerite becomes metamict with time, lead is often trapped in nanometric galena
642 (Fig. 5; Lumpkin *et al.* 2012). Furthermore, Macmillan *et al.* (2017) suggest that galena
643 can also be (1) cogenetic with brannerite; (2) a product of the recrystallization of early
644 Pb-rich brannerite; (3) a product of uraninite dissolution. The issue of U loss in altered
645 domain (Fig. 8) and the presence of exsolution of U-rich nanodomains (Fig. 5a-c) in
646 brannerite, are also of primary importance for geochronological purposes. Accurate
647 interpretation of ages, obtained either by bulk (ID-TIMS) or high resolution in-situ
648 techniques (SIMS, LA-ICPMS) requires the petrogenesis and chemistry of both brannerite
649 and associated phases, from the microscale down to the nanoscale to be determined.

650

651 *Recovery of U and other elements from natural brannerite*

652

653 While brannerite has been explored as a matrix storage for nuclear wastes (*e.g.*
654 Lumpkin, 2001), its refractory nature to leaching has been recently challenged in order to
655 evaluate potential uranium recovery (*e.g.* Lottering *et al.*, 2008, Charalambous *et al.*, 2014;
656 Gilligan and Nikoloski, 2015a,b). Based on tests made on natural and synthetic crystals,
657 these authors have shown that several parameters can influence the recovery rates such
658 as temperature, pH, and Fe³⁺ concentrations in the solvents. This last parameter is very
659 important, as the amount of extracted U from brannerite is proportional to the Fe³⁺
660 concentration (Gogoleva *et al.*, 2012; Charalambous *et al.*, 2013, 2014). Iron substitutes
661 for titanium in the B site and its abundance, which varies between samples, depends on
662 the genetic types of brannerite (Figs. 11b, 12c). The high Fe content of some pegmatitic
663 occurrences (Namibia) makes them good candidates for naturally magnifying U recovery.
664 However, these ores are generally complex and brannerite also contains other elements
665 such as Ca, REE and Si (Fig. 12a). While leaching mechanisms remain unknown, it appears
666 that when uranium is partially replaced in the brannerite structure by other elements (Ce,
667 Ca...), the extraction of uranium is reduced (Charalambous *et al.*, 2010). Hence, several
668 elements that could represent economically interesting co-products (*e.g.* REE) may also
669 represent a limit for acceptable recovery rates of uranium from brannerite

670

671 **Conclusion**

672

673 Based on original analytical data from a variety of brannerite occurrences, this
674 study demonstrates that chemical contents and REE abundances of brannerite reflect the
675 geological conditions of their formation. Combining both results, it is possible to obtain a
676 reliable geochemical classification at the scale of ore locality and genetic types. Such

677 fingerprints are useful for forensic science, the exploration industry, understanding
678 metallogenic process and optimizing extraction of uranium. Our dataset is not exhaustive
679 though, and it is necessary to complement it with other occurrences from other genetic
680 environments, such as uraniferous conglomerates (e.g. Elliot lake, Witwatersrand) or
681 metamorphic domains (Domes Region in Zambia). Applying our approach also requires
682 not only blind spot analyses, but a careful preliminary study or ore petrography, as
683 brannerite ores can be polyphase and chemically complex.

684 This study also points out the partial misunderstanding of various geochemical
685 processes at the atomic scale. One of the major points is the valence state of U, its origin
686 (e.g. the role of redox conditions for brannerite formation) and the major consequences
687 for the present complex mineral chemistry of brannerite. Itself, the presence of uranium
688 has severe effects on brannerite crystal structure and the metamict aspect of variously
689 aged natural brannerite was demonstrated (e.g. Lumpkin *et al.*, 2012). This may be
690 responsible for the origin of various crystal defects, which may represent possible non-
691 stoichiometric traps for a variety of elements (e.g. Si). How to reconcile such
692 crystallographic self-alteration with the apparent pristine mineral geochemistry is not
693 therefore straightforward. Further study on natural brannerite is required to follow this
694 holistic approach and to combine various scale observation and techniques, in order to
695 meet such a challenge.

696

697 **Acknowledgements**

698

699 This article was part of the UTILE multi-disciplinary project and was sponsored by the
700 NEEDS (CNRS-AREVA-CEA) program. We greatly thank Olivier Rouer (GeoRessources,
701 Nancy), Martin Robyr (Univ Lausanne), Philippe de Parseval (centre de

702 microcaratérisation Raimond Castaing, Toulouse) for EPMA analyses and mapping and
703 Nadia Guignard (IC2MP, Poitiers) for Raman spectrometry. We express our gratitude to
704 Lubos Vrtiska (Narodni Museum, Prag), Michel Cuney (GeoRessources), Jean-Claude
705 Leydet and Marc Brouand (Orano) for providing a part of the samples. We thank Roger
706 Mitchell and Jason Harvey for handling the manuscript and three anonymous reviewers
707 for their constructive comments, which helped to significantly improve the manuscript.

708

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993 Figure captions

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995 FIG. 1. Crystal structure of Brannerite, down the b axis (modified after Mesbah *et al.*,
996 2019).

997 FIG. 2. Map showing the location of studied brannerite sample and their genetic type.

998 FIG. 3. Back-Scattered Scanning Electron (BSE) images of studied hydrothermal
999 brannerite: (a) brannerite from La Gardette, associated with Cu-Bi sulphides and
1000 surrounded by a corroded grain boundary; (b) altered (upper right corner) and unaltered
1001 brannerite from Bou Azzer. The location of Focused Ion Beam (FIB) foil cut across
1002 unaltered brannerite is reported; (c) detailed view of altered Bou Azzer brannerite
1003 characterized by a complex association U-rich and U-poor domains. Note the presence of
1004 radial fractures filled with coffinite around altered brannerite; (d) stockwork with early
1005 brannerite (Br I) crosscut by two successive brannerite veins (Br II and Br III) from
1006 Himalaya; (e) partly altered (light grey) brannerite crystal from Mont Chemin; (f)
1007 brannerite from Kratka wValley, associated with undetermined Ti oxides and minute
1008 uraninite inclusions. The location of Raman analyses (R) is reported for each brannerite
1009 sample. Abbreviations: Ab: Albite; Ang: Anglesite; Brn: Brannerite; Cer: Cerussite; Cof:
1010 Coffinite; Gn: Galena; Qz: Quartz; Urn: Uraninite.

1011 FIG. 4. (a) to (d) qualitative EDS-SEM X-ray chemical maps of brannerite crystals from Bou
1012 Azzer occurrence; (e) to (h) quantitative FE-EPMA element distribution maps from
1013 Himalaya occurrence.

1014 FIG. 5. Transmission Electron Microscope (TEM) and Scanning TEM (STEM) images from
1015 a FIB foil cut across a brannerite crystal from Bou Azzer: (a) TEM Bright Feld (BF) image
1016 showing the abundance of U-rich and more rarely Pb-rich inclusion within brannerite
1017 (Brn). Inset corresponds to Selective Area Electron Diffraction (SAED) pattern from

1018 brannerite full with U-rich inclusions and demonstrates its amorphous state; (b) STEM
1019 HAADF (High Angle Annular Dark Field) (STEM-DF) image of a zoom from area shown in
1020 A. In this mode, bright areas correspond to high density materials (e.g. U-rich or Pb-rich
1021 inclusion) or thicker regions. The white rectangle indicates location of EDS chemical
1022 maps; (c) to (e) U, Ti and Pb chemical maps from the same area, revealing the presence of
1023 Pb and U-rich domains;

1024 FIG. 6. Back-Scattered Scanning Electron (BSE) images of studied pegmatitic brannerite;
1025 (a) brannerite monocrystal from Crocker's Well, showing pervasive cracking and
1026 chemical zoning due to variable Th enrichment; (b) brannerite from Hidden Valley
1027 exhibiting altered domains along fracture (dark grey), uraninite inclusions and a complex
1028 corroded boundary; (c) brannerite from El Cabril with uraninite inclusions and pervasive
1029 corrosion along grain margins; (d) brannerite from El Cabril showing partial replacement
1030 by secondary uraninite, Ti oxide and unknown Y-rich minerals (see Fig. 6d); (e) partly
1031 altered brannerite from Lodrino pegmatite. The location of Focused Ion Beam (FIB) foil
1032 cut across unaltered brannerite is reported; (f) secondary uranium minerals developing
1033 along cracks in brannerite from NA12 pegmatite (Namibia). The location of Raman
1034 analyses (R) is reported for each brannerite sample. Abbreviations: Brn: Brannerite; Cof:
1035 Coffinite; Kfs: K-feldspar; Urn: Uraninite.

1036 FIG. 7. Quantitative FE-EPMA element distribution maps from El Cabril occurrence.

1037 FIG. 8. Transmission Electron Microscope (TEM) and Scanning TEM (STEM) images from
1038 a FIB foil cut across a brannerite crystal from Lodrino (a to e): (a) TEM-BF image, showing
1039 the presence of altered domains within unaltered brannerite. Selected Area Electron
1040 Diffraction (SAED) patterns from unaltered brannerite (inset in the top) also supports the
1041 amorphous state of brannerite, while SAED pattern from altered brannerite (inset in the
1042 bottom) indicate the presence of nanocrystalline domains (possibly coffinite); (b) STEM-

1043 DF image of a zoom in the same area; (c) to (e) U, Ti and Si chemical maps from the same
1044 area, demonstrating depletion or enrichment in the altered domain relative to the
1045 unaltered domain. Brn: brannerite.

1046 FIG. 9. Boxplots of major and minor element contents for each studied brannerite sample,
1047 considering its genetic type. Contents are given in apfu calculated on a basis of 6 oxygen
1048 atoms from EPMA results (Table 1). For Y, abundances obtained by LA-ICPMS
1049 measurement and available in Table 2 are reported. Dashed line represents the
1050 theoretical U and Ti contents of ideal UTi_2O_6 brannerite.

1051 FIG. 10. Boxplots of trace element abundance measured by LA-ICPMS for each studied
1052 brannerite sample, considering the hydrothermal (blue) and pegmatitic (red) genetic
1053 types.

1054 FIG. 11. Principal component analysis of the EPMA dataset of major and minor element
1055 contents in brannerite from diverse genetic types. Left frames: spot analyses (*i.e.*
1056 individuals) plotted on the PC1 (Dim1) vs. PC2 (Dim2) plane, with respective percentage
1057 that explain the element content variability. Right frames: elements (*i.e.* variables) plotted
1058 in the same plane.

1059 FIG. 12. Binary diagrams of selected A site cations versus calculated U^{4+} content (a) to (c)
1060 and average U valence (d) to (f) of brannerite in atoms per formula unit (apfu). Details for
1061 calculation of U^{4+} content and average U valence are provided in the material and methods
1062 section, following Collela *et al.* (2005). Since only Y and Ce were measured by EPMA, it is
1063 not possible to draw a trend curve for substitution (4).

1064 FIG. 13. Binary diagram of selected B site cations versus Ti content (a) and average U
1065 valence of brannerite (b) in atoms per formula unit (apfu).

1066 FIG. 14. Binary and ternary plots, illustrating the substitution rates at sites A and B and
1067 the relative proportions of substituents: (a) Ternary plot, including Si abundance and

1068 showing discernible substitution type and rate depending on brannerite genetic types; (b)
1069 Ternary plot showing the relative proportion of each major A site substituents and (c) Fe
1070 versus Al content in brannerite, showing various occupancy of B site (excluding Ti)
1071 depending on genetic type and redox conditions.

1072 FIG. 15. Synoptic chart illustrating the results of two-sample Kolmogorov-Smirnov test.
1073 For each element, its distribution was compared between two samples (locality or genetic
1074 type). The more red coloured cases there are, the more significant differences in mineral
1075 chemistry between samples there are.

1076 FIG. 16. Chondrite-normalized REE patterns from brannerite (a) to (b) and associated
1077 uranium phases (c) from hydrothermal and pegmatitic types. Normalisation values are
1078 from McDonough and Sun (1995).

1079 FIG. 17. Total REE versus chondrite normalised light over heavy REE for brannerite of
1080 hydrothermal and pegmatitic types. Normalisation values are from McDonough and Sun
1081 (1995).

1082

1083 TABLE 1. Compositional data from EPMA analyses for brannerite of hydrothermal, and
1084 magmatic genetic types. * Fe₂O₃ recalculated from FeO. SD: Standard deviation. n.d.: not
1085 detected. SD: Standard Deviation.

1086

1087 TABLE 2. Trace Element data from LA-ICPMS analyses for brannerite of hydrothermal,
1088 and magmatic genetic types. (Σ LREE)_N = La_N+Ce_N+Pr_N+Nd_N+Sm_N; (Σ HREE)_N =
1089 Er_N+Tm_N+Yb_N+Lu_N.^N for chondrite-normalised. n.d.: not detected. SD: Standard
1090 Deviation.

1091

1092

1093 Appendix - Geological setting of studied brannerite samples

1094

1095 *Geological setting of hydrothermal brannerite*

1096

1097 La Gardette Mine (GD) is located in Western French Alps close to Bourg-d'Oisans
1098 city. Alpine-type quartz veins crosscut the amphibolite of the Variscan basement and its
1099 Triassic carbonate cover (Debelmas *et al.*, 1972). Ore minerals include native gold, galena,
1100 pyrite, chalcopyrite, tennantite and brannerite (Geffroy, 1963). Age of mineralization is
1101 currently unknown but it could be related to Upper Miocene (ca. 5-11 Ma) episodes of
1102 hydrothermal fluid circulation recorded in the Belledonne Massif to the Northwest
1103 (Gasquet *et al.*, 2010).

1104 The Bou Azzer (BA) deposit is located in the Moroccan Anti Atlas Belt. It occurs
1105 within a Proterozoic ophiolitic unit covered by unconformable Palaeozoic sedimentary
1106 rocks (Leblanc and Billaud, 1982). Bou Azzer is classified as a particular case of Five-
1107 Element Vein-Type deposits (Leblanc, 1986; Kissin, 1992); it is currently mined for Co Ni,
1108 Ag and Au. The polyphase mineralization includes an early Ni-Co-Fe arsenide stage
1109 followed by a late Cu-Zn-Fe sulfide stage (Ennaciri *et al.*, 1997) related to high salinity
1110 brines (Leblanc and Lbouabi, 1988). While uraninite is present throughout the whole
1111 mineralization evolution, brannerite only occurs during the latest stage in association
1112 with molybdenite, chlorite, and quartz (Ennaciri, 1995). Brannerite stage has been dated
1113 by U-Pb LA-ICPMS method at 310 ± 5 Ma (Oberthür *et al.*, 2009).

1114 Brannerite (HL) was collected in the Chhuling Khola Valley in Nepal. This area
1115 consists of a series of schists, gneisses, and migmatites that belong to the Greater
1116 Himalayan Sequence, which is thrust over the low-grade metamorphic rocks of the
1117 Lesser Himalayan Sequence, along the Main Central Thrust (Pêcher, 1989). Among these

1118 high-grade gneisses, an albitized and U-mineralized zone is exposed (Maruejol, 1988).
1119 While biotite gneisses have recorded an early sodic metasomatic stage coeval with ductile
1120 deformation along the MCT, brannerite co-precipitated with secondary albite in brittle
1121 veins forming a stockwork zone. Formation of brannerite is considered as the result of
1122 alteration of Ti oxides of the biotite gneisses by Na-U alkaline and oxidizing fluids
1123 (Maruejol, 1988) under low-grade metamorphic conditions. Isotope Dilution thermal
1124 ionization mass spectrometry (ID-TIMS) U-Pb dating on brannerite has given a
1125 crystallization $^{206}\text{Pb}/^{238}\text{U}$ age at 4.8 Ma (Copeland *et al.*, 1991).

1126 The Mont Chemin (MC) mines are located in the eponymous mountain in Western
1127 Valais, Switzerland. The mines have been exploited from Middle Age until to the 20th
1128 century for Au, Ag, Pb, Fe, and fluorite (Ansermet, 2001). The veins crosscut the
1129 metamorphic Variscan basement (external crystalline massif) and particularly small late
1130 Palaeozoic granite intrusions within gneisses. At the Tête des Econduits, quartz veins
1131 include scheelite, anatase, fluorite, native Au, and brannerite (Meisser, 1998). These
1132 Alpine-type veins are probably related to a regional Miocene episode of hydrothermal
1133 fluid circulation at *ca* 10 Ma (Marshall *et al.*, 1998).

1134 The Kratka Valley (KV) occurrences are located to the north of Gemerska Poloma
1135 between Dobsina and Kosice in Eastern Slovakia. U-bearing quartz veins occur within the
1136 Ordovician Vlachovo Formation of the Southern Gemericum Unit (Vozarova *et al.*, 2010).
1137 This volcano-sedimentary sequence was further intruded by Permian granites, covered
1138 by Mesozoic sediments and affected by Cretaceous regional metamorphism (Vozarova *et*
1139 *al.*, 2014). A wide range of U mineralization is found within the Gemericum Unit, including
1140 U-Mo mineralized horizons, stratiform Cu-U redbeds and U-Mo stockworks (Rojkovic *et*
1141 *al.*, 1993). U-Ti oxides, including brannerite, were reported from several localities
1142 (Rojkovic and Boronikhin, 1982). At Kratka Valley, brannerite-bearing quartz veins also

1143 contain gold, arsenopyrite, chalcopyrite, molybdenite, pyrite, rutile, uraninite as well as
1144 many secondary U minerals. Timing of brannerite formation is currently unknown, but
1145 Lower Jurassic (Stevko *et al.*, 2014) and Lower Cretaceous (Rojkovic *et al.*, 1993)
1146 mineralizing events have been reported in the area.

1147

1148 *Geological setting of pegmatitic brannerite*

1149

1150 The Crocker's Well (CW) prospect, located in the southern part of Central Australia
1151 is a uranium occurrence discovered in 1951. Ore is hosted by peraluminous sodic
1152 granitoids, mainly adamellite and trondhjemite, and minor sodic gneisses (Ashley, 1984,
1153 and reference therein). Emplacement of this suite has been dated by zircon ID-TIMS
1154 (isotopic Dilution Thermal ionization Mass spectrometry) U-Pb at 1579.2 ± 1.5 Ma
1155 (Ludwig and Cooper, 1984). Although the distribution of brannerite is controlled by
1156 fractures (Campana and King, 1958), the vein systems and the mineralized breccia are
1157 restricted to the host granite, which did not experience hydrothermal alteration.
1158 Brannerite is associated with quartz, F-bearing phlogopite, sodic plagioclase, fluorapatite,
1159 niobian rutile, monazite, muscovite, chlorite, tourmaline, and fluorite (Ashley, 1984).
1160 Brannerite formation probably results from the evolution of a late peraluminous
1161 magmatic system, as indicated by the younger $^{206}\text{Pb}/^{238}\text{U}$ ages obtained directly on
1162 brannerite (550-572 Ma, Ludwig and Cooper, 1984). In this sense, Crocker's Well uranium
1163 occurrence shares many analogies with Rössing and Limousin types (*e.g.* Cuney, 2010),
1164 with the exception of the sodic enrichment.

1165 The Hidden Valley (HV) area is located at Brannerite Hill in the North Finders
1166 Ridge in south Central Australia. This area is characterized by Mesoproterozoic
1167 migmatitic gneisses associated with Neoproterozoic metasediments and volcanics (Coats

1168 and Blissett, 1971), which recorded metamorphism related to the Delamerian orogeny
1169 (Foden *et al.*, 2006). Palaeozoic leucogranites and pegmatites dated around 450 Ma are
1170 intrusive within this metamorphic sequence (Wülser, 2009). Among the pegmatite
1171 intrusions, one displays an alkaline syenite composition and includes albite, K-feldspar,
1172 quartz, biotite, alkaline amphibole and brannerite (Wülser, 2009). Other brannerite
1173 occurrences (not studied) are within quartz-ilmenite veins such as Charlotte and Jacob
1174 mineralizations characterized by large euhedral brannerite crystals (Wülser, 2009).

1175 The El Cabril (EC) occurrence is located in the Sierra Albarrana, Andalusia (Spain).
1176 This massif belongs to the late Proterozoic to Lower Cambrian Ossa Morena zone and is
1177 mainly composed of paragneisses, micaschists and garnet-bearing amphibolites
1178 (González del Tánago and Arenas, 1991; Azor and Ballèvre, 1997). Metamorphic rocks are
1179 cross cut by pegmatite intrusions, which are composed of quartz, K-feldspar, albite,
1180 muscovite, tourmaline, garnet, biotite, monazite, ilmenite, rutile and primary uranium
1181 minerals, such as brannerite and uraninite (Garotte *et al.*, 1980; Contreras *et al.*, 1983).
1182 Age of brannerite crystallization is unknown but is not older than the Devonian thermal
1183 event (351Ma - 391Ma) recorded by amphibolite and metapelite in the Sierra Albarrana
1184 (Dallmeyer and Quesada, 1992).

1185 The Lodrino (BR1) pegmatite in Ticino, Switzerland crosscuts the Variscan
1186 orthogneisses of the Leventina Nappe (Rütti *et al.*, 2008) and is mainly composed of
1187 quartz and orthoclase, with minor albite, muscovite, brannerite, molybdenite, scheelite,
1188 apatite, titanite, powellite and rutile (Bianconi and Simonetti, 1967). Age of pegmatite
1189 emplacement is unknown, but it is probably related to the well-known Tertiary pegmatite
1190 field that extends over Southwestern Switzerland (Wenk, 1970; Burri *et al.*, 2005). This
1191 area overlaps the zone of alpine migmatization and available U-Pb geochronological
1192 constrains span between 29 and 20 Ma (Guastoni *et al.*, 2014). This age is significantly

1193 older than the K-Ar age at ca. 11.4 Ma reported for the Lengenbach brannerite
1194 mineralization in Eastern Valais (Purdy and Stalder, 1973; Graeser and Guggenheim,
1195 1990).

1196 Sample NA12 is a single crystal from a pegmatite collected along the Marienfluss
1197 Valley, to the West of Hartmann Mountains, Northern Namibia. This pegmatite is intrusive
1198 within the Paleoproterozoic Epupa Metamorphic Complex, made of migmatized granitoid
1199 gneisses with rare intercalations of metasediments (Kröner *et al.*, 2010). This unit was
1200 intruded by Mesoproterozoic granitoids related to extension in the Southern Congo
1201 craton (Kröner and Rojas-Agramonte, 2017) and further experienced further
1202 overprinting due to the late Neoproterozoic to early Palaeozoic Pan-African event related
1203 to the Kaoko orogeny (Goscombe *et al.*, 2003). This later event, characterized by
1204 polyphase deformation and magmatism has produced biotite-muscovite pegmatite dykes,
1205 especially in the Hartmann Mountains (Goscombe *et al.*, 2005); sample (NA12) is spatially
1206 related to this ca. 500 Ma episode (Goscombe *et al.*, 2005), but further studies are required
1207 to confirm this hypothesis.

1208

1209 TABLE A1 Standard used for calibration of EPMA analyses.

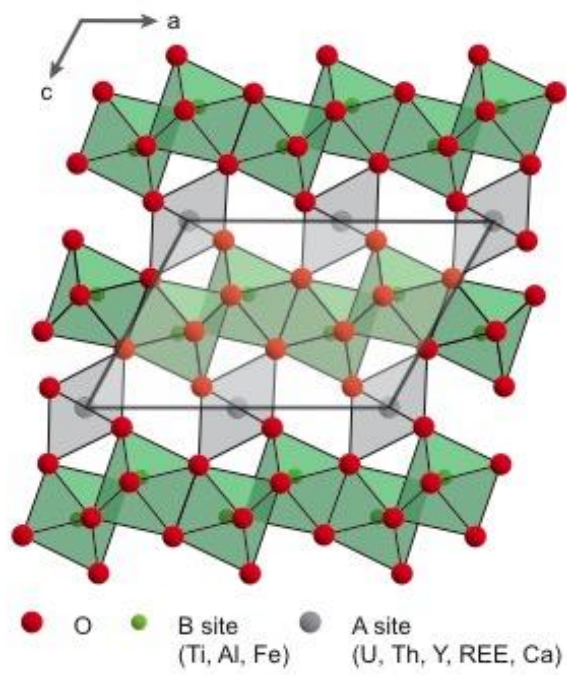
1210

1211 FIG. A1 Raman spectra of a synthetic brannerite and studied natural brannerite samples.
1212 The synthetic brannerite sample comes from Mesbah *et al.* (2019). The characteristic
1213 vibrational Raman modes of synthetic brannerite are at 760 cm⁻¹ (antisymmetric
1214 stretching vibration of the (Ti-O-Ti) moiety), 195, and 159 cm⁻¹ (lattice external modes,
1215 see Zhang *et al.* (2013) and Mesbah *et al.* (2019) for a complete assignment of the Raman
1216 vibration modes). Spectra of natural samples were acquired in unaltered domain (Figs
1217 3,6). Abbreviations: BA: Bou Azzer; KV: Kratka Valley; MC: Mont Chemin; HL: Himalaya;

1218 GD: La Gardette; NA12: Namibia; CW: Crocker's Well; EC: El Cabril; HV: Hidden Valley;

1219 BR1: Lodrino.

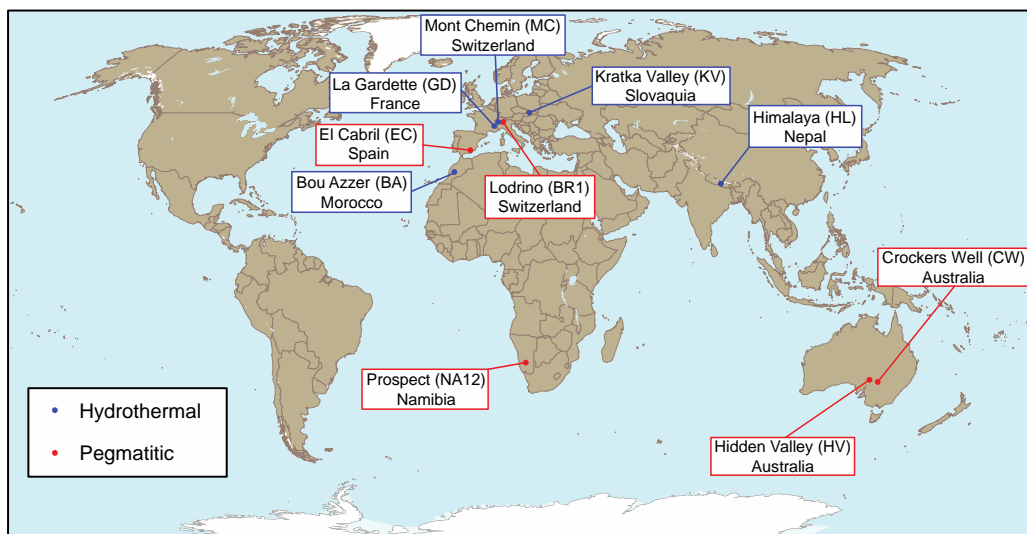
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1222 Figure 1

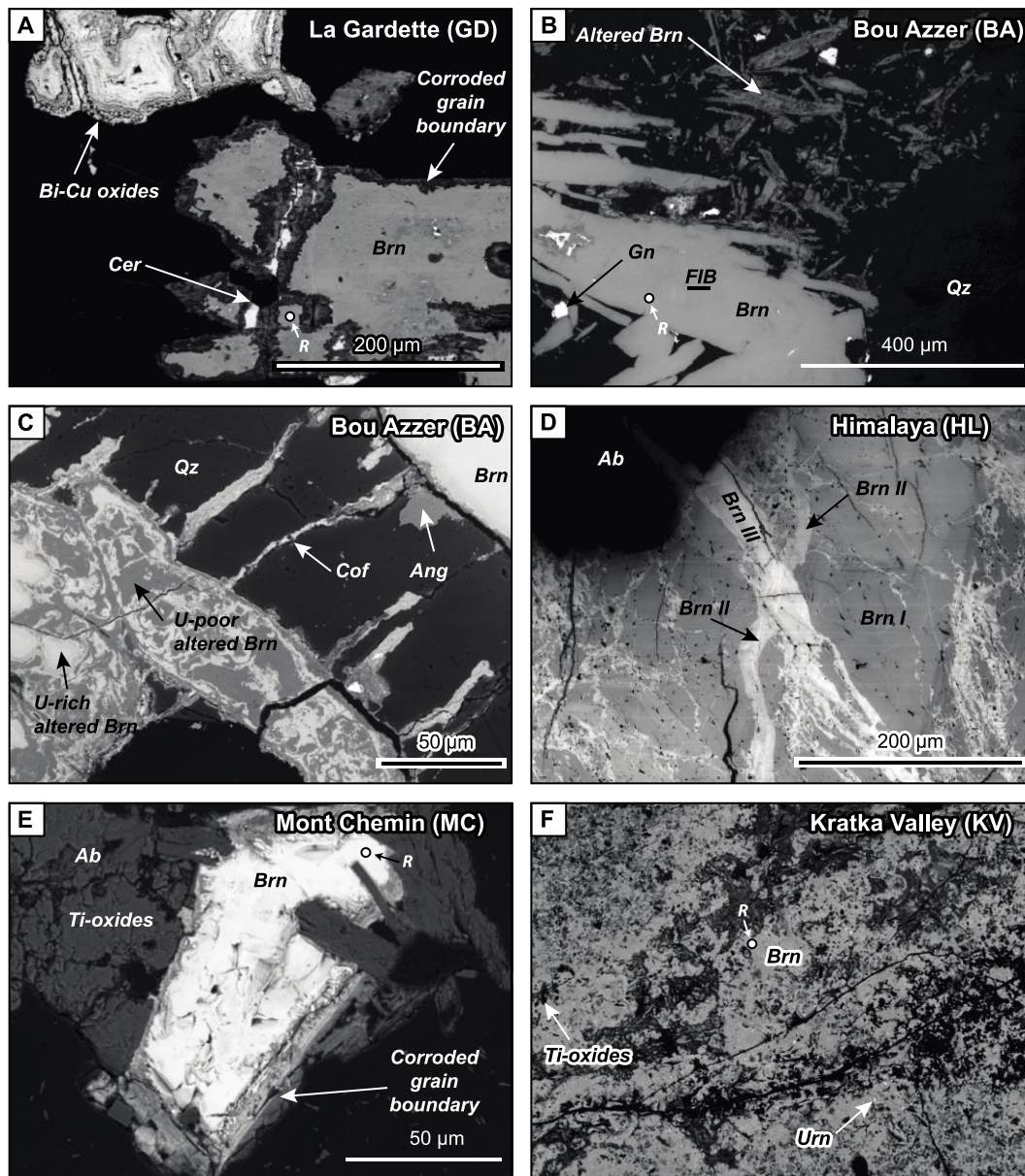
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1225 Figure 2

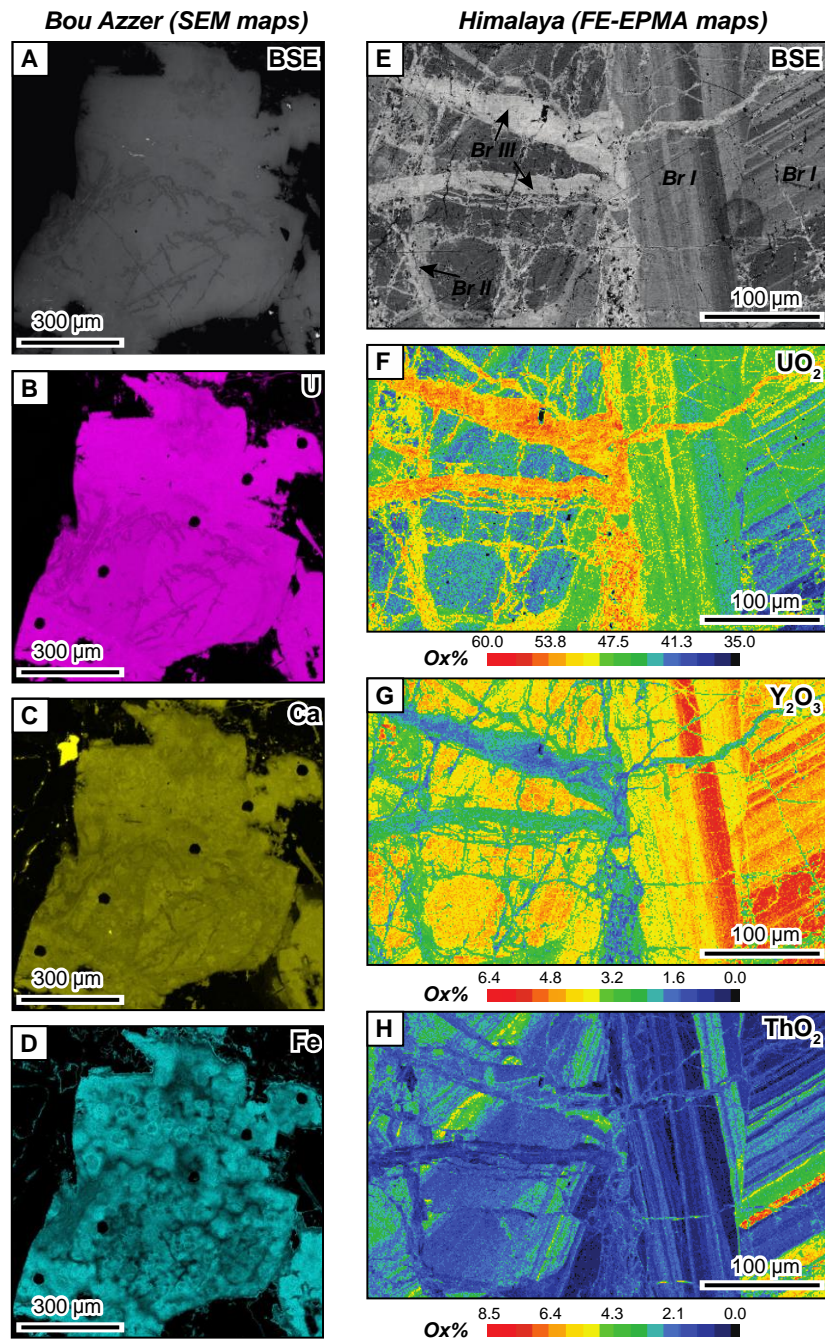
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1228 Figure 3

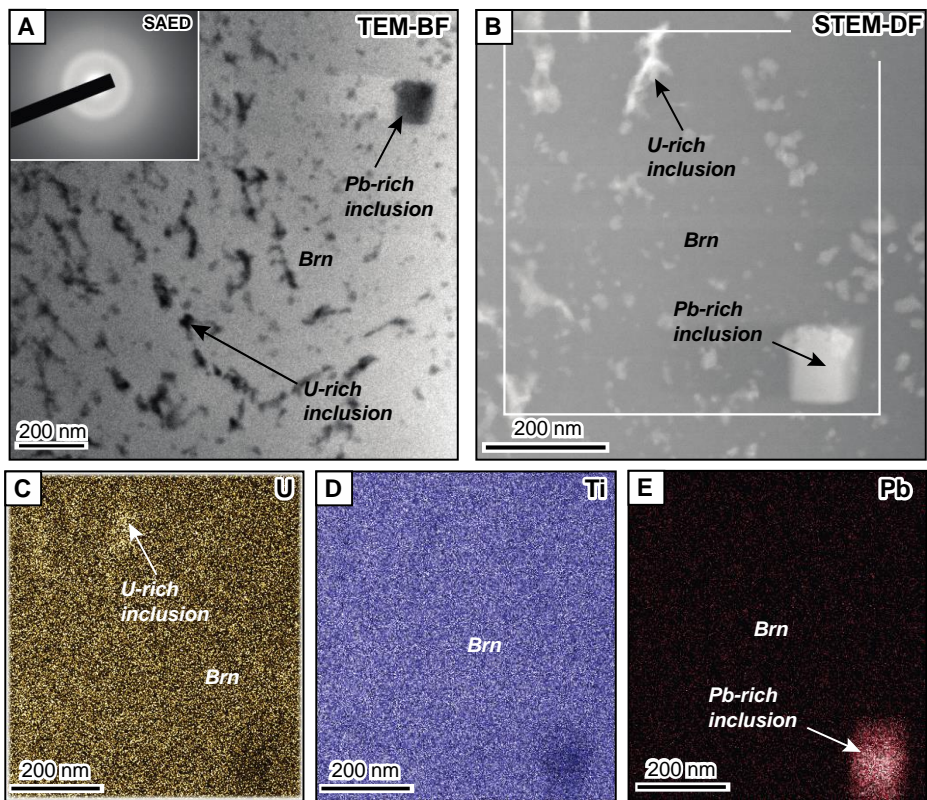
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1231 Figure 4

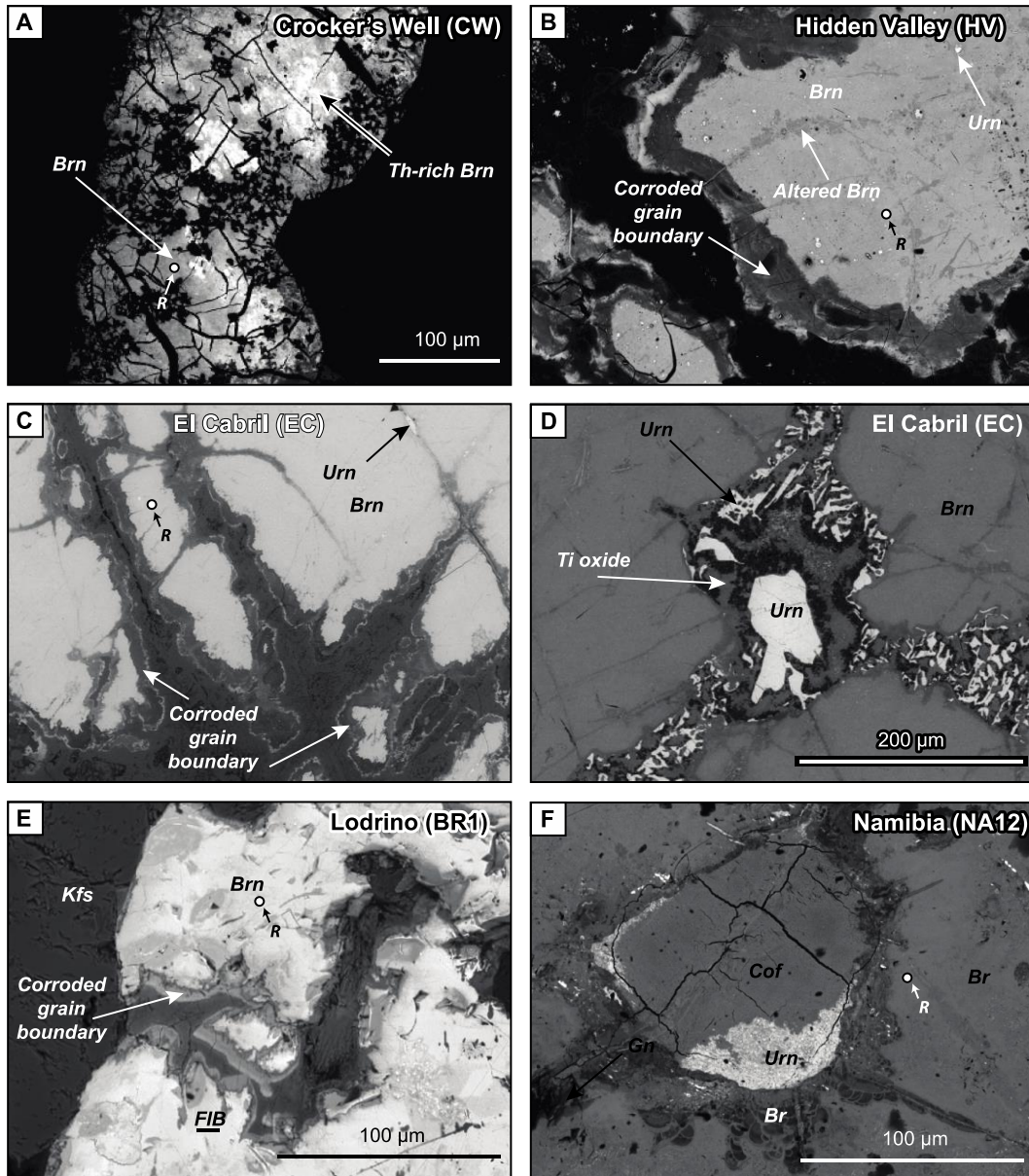
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1234 Figure 5

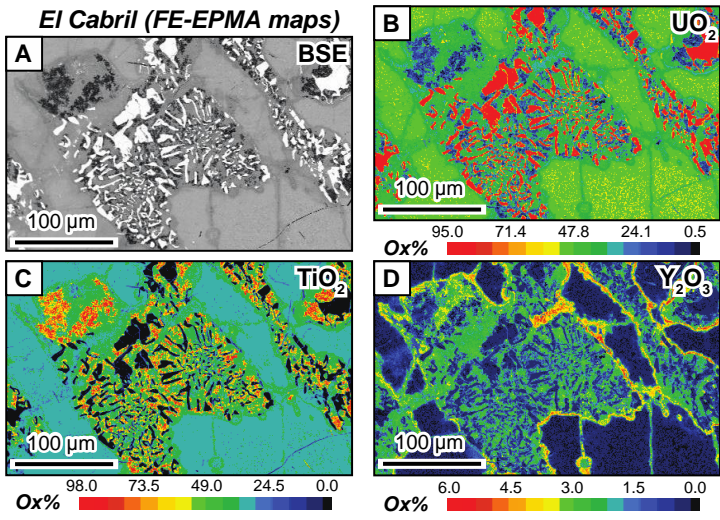
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1237 Figure 6

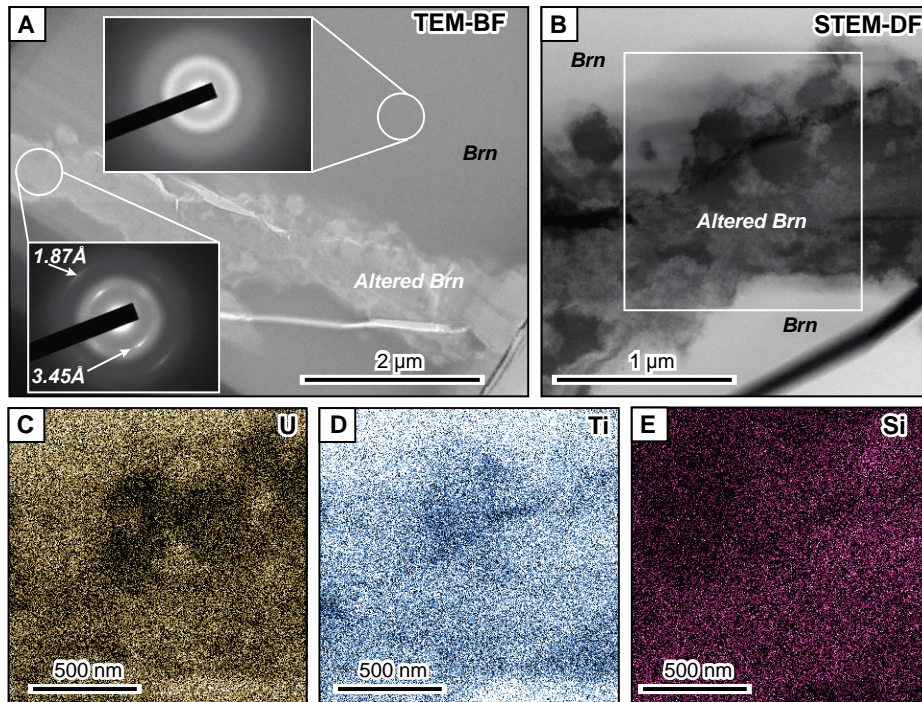
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1240 Figure 7

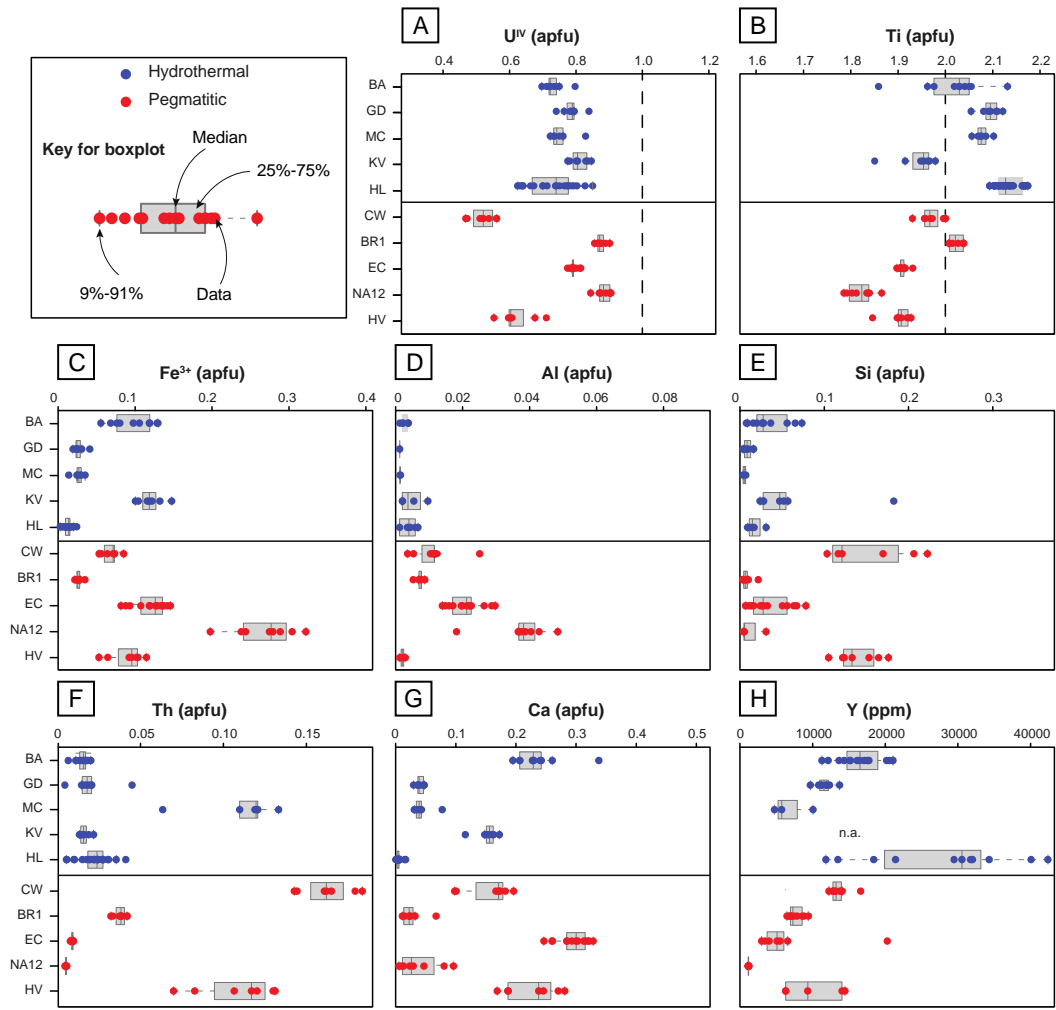
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1243 Figure 8

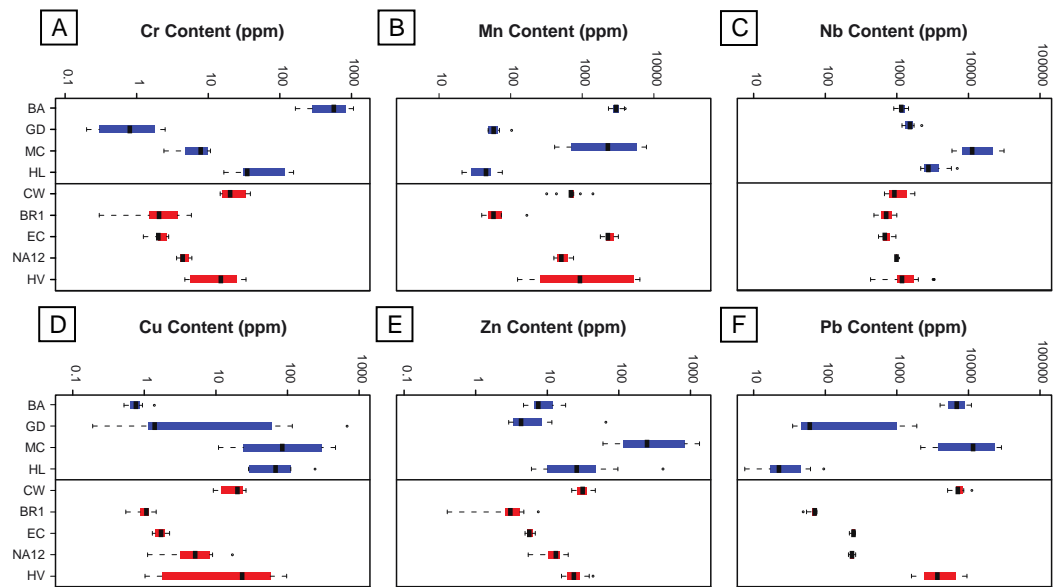
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1246 Figure 9

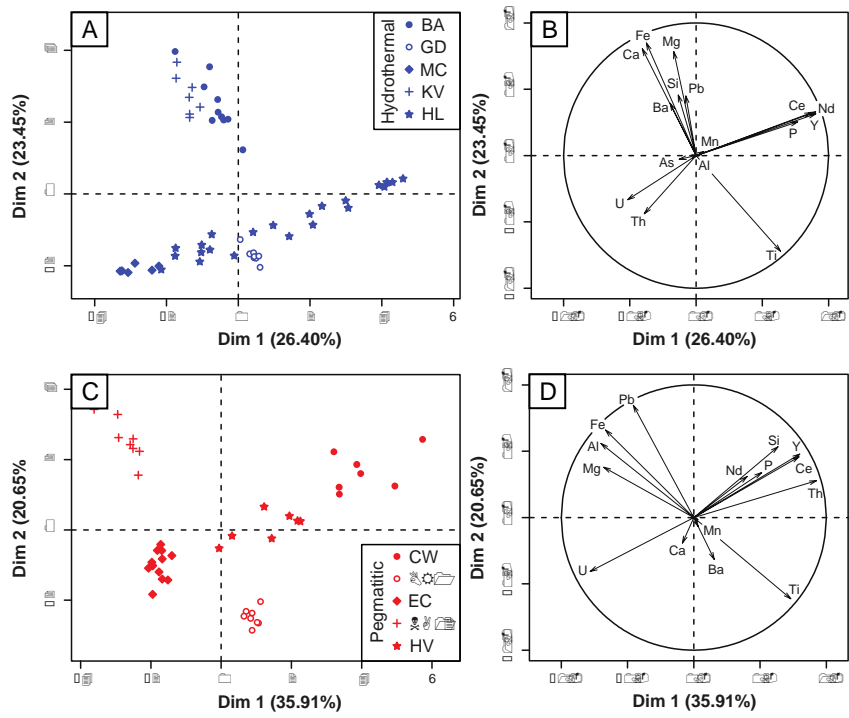
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1249 Figure 10

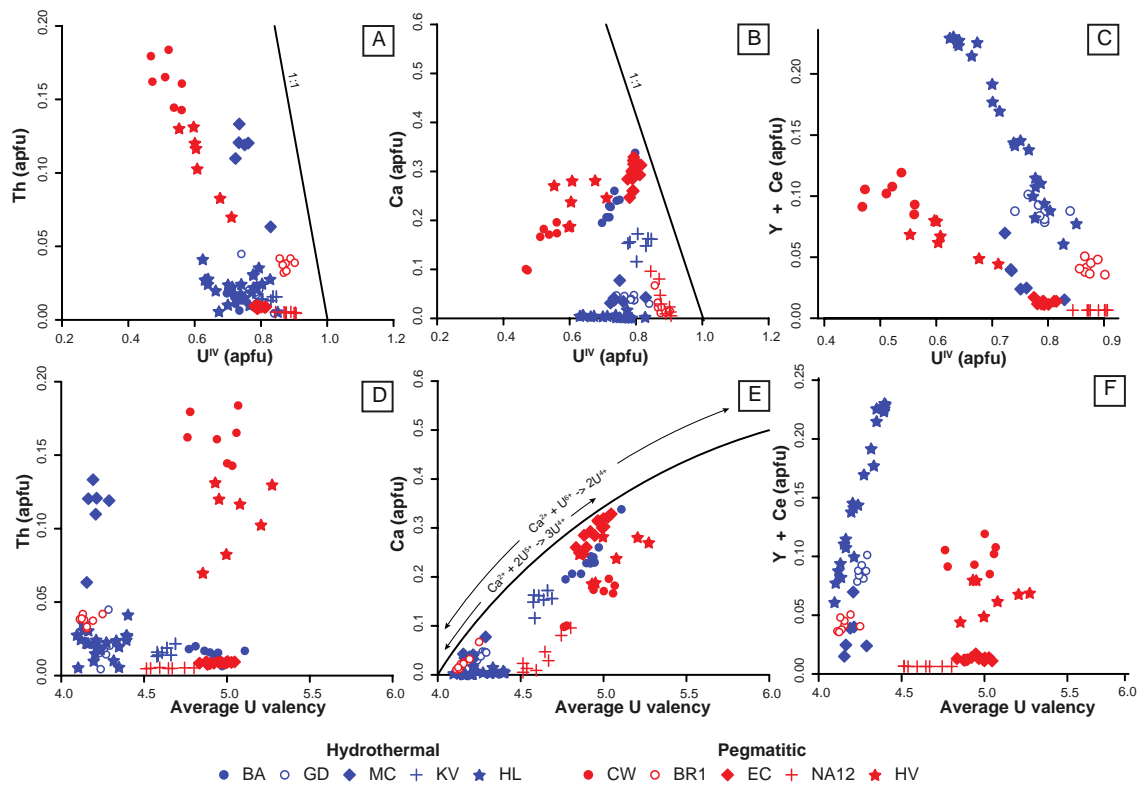
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1252 Figure 11

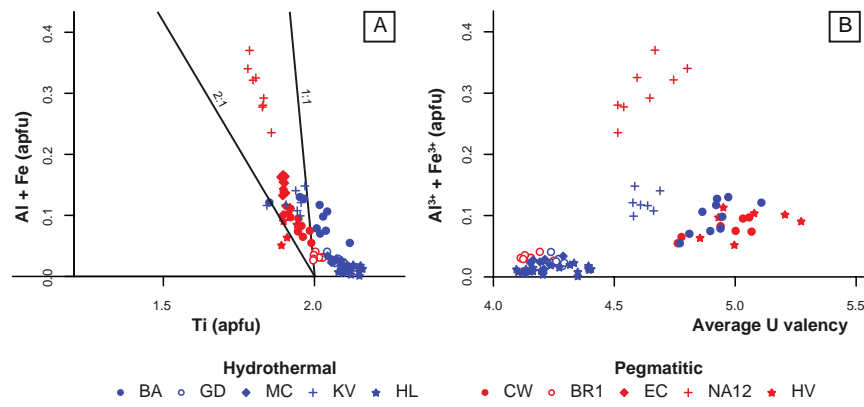
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1255 Figure 12

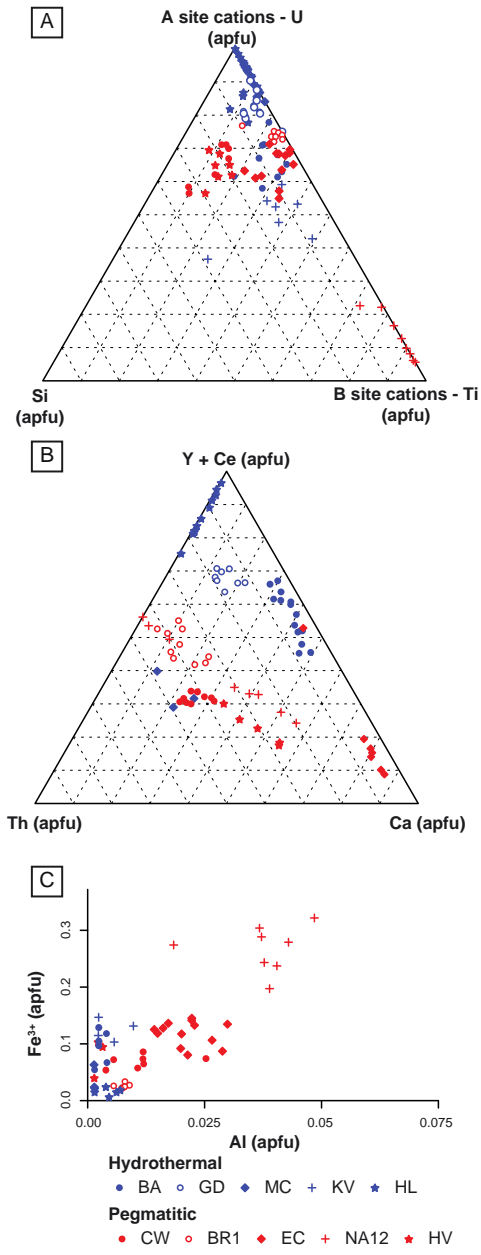
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1258 Figure 13

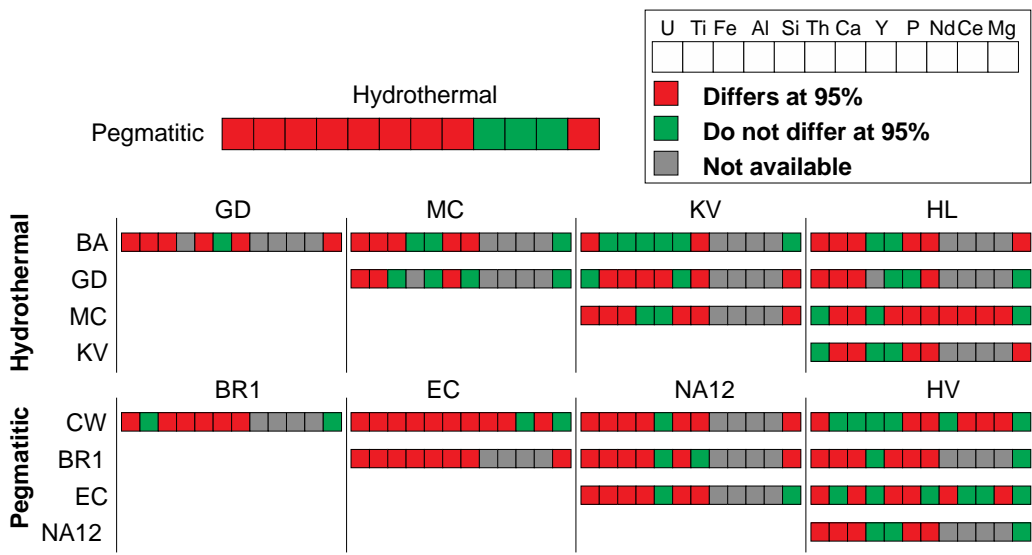
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1261 Figure 14

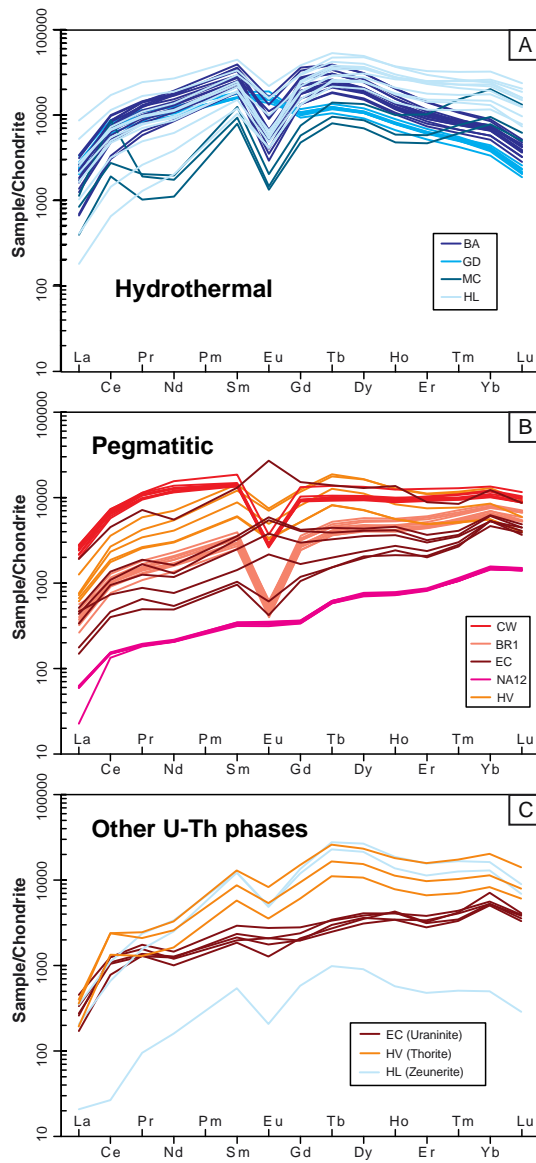
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1264 Figure 15

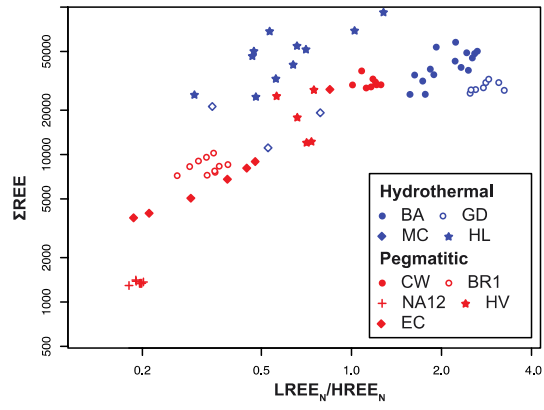
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1267 Figure 16

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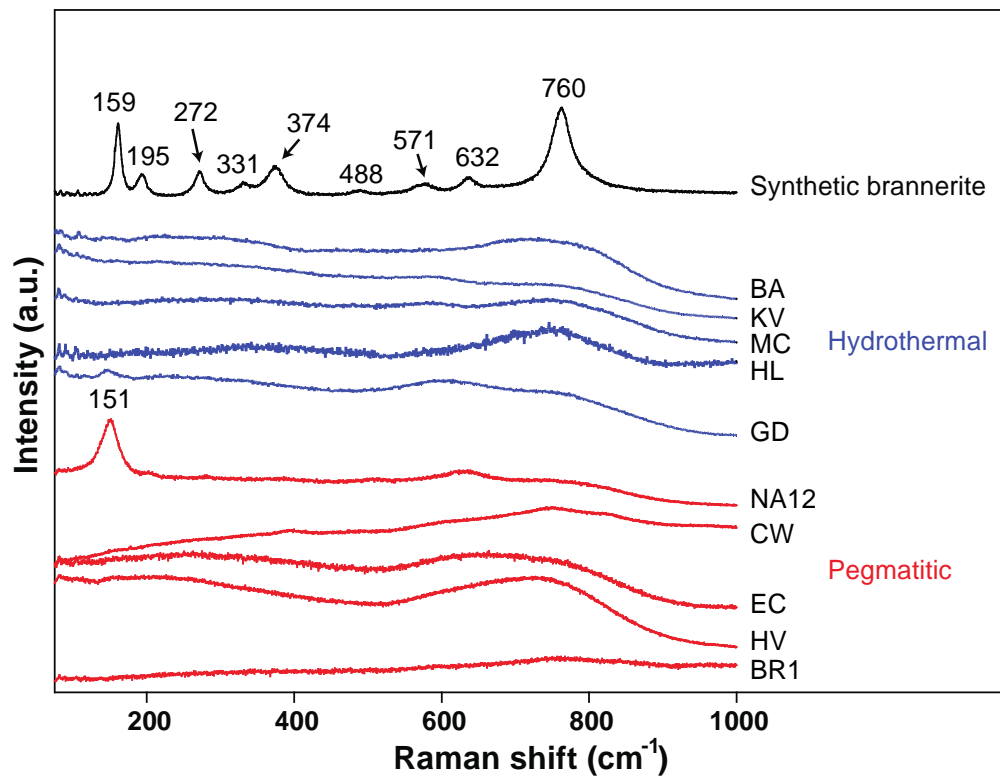
1270 Figure 17

1271

Element	Standard formula	Diffraction Crystal	Analyzed radiation line	Counting time for peak (s)
U	UO ₂	PET	Mα	20
Ti	MnTiO ₃	LPET	Kα	20
Si	Albite	TAP	Kα	10
Al	Al ₂ O ₃	TAP	Kα	10
Fe	Fe ₂ O ₃	LIF	Kα	20
Ca	Andradite	PET	Kα	20
Ba	BaSO ₄	LIF	Lα	20
Mn	MnTiO ₃	LIF	Kα	20
Mg	Olivine	TAP	Kα	20
Y	YPO ₄	TAP	Lα	20
Ce	CePO ₄	LPET	Lα	20
Nd	NdPO ₄	LIF	Lα	20
Pb	PbS	LPET	Mα	20
Th	ThO ₂	PET	Mα	20

1278
1279
1280

Figure A1



1281
1282 Figure A1