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Nb-Ta fractionation in peraluminous granites: a marker of the magmatic-hydrothermal transition --Manuscript Draft--

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Abstract:	<p>In their late stages of evolution, peraluminous granitic melts exsolve a large amounts of fluids which can modify the chemical composition of granitic whole rocks samples. The Nb/Ta ratio is expected to decrease during magmatic differentiation of granitic melts, but the behavior of both elements at the magmatic-hydrothermal transition remains unclear. Using a compilation of whole rock geochemical data available in the literature, we demonstrate that fractional crystallization alone is not sufficient to explain the distribution of Nb-Ta in most peraluminous granites. However, we notice that most of the granitic samples displaying evidence of interactions with fluid, regardless of their age or their emplacement conditions, have Nb/Ta < 5. We propose that the decrease of the Nb/Ta ratio in highly evolved melts is the consequence of both fractional crystallization and sub-solidus magmatic-hydrothermal alteration. We suggest that the value Nb/Ta = 5 in peraluminous granite fingerprints the magmatic-hydrothermal transition. Furthermore, a Nb/Ta ratio of 5 appears to be a good marker to discriminate mineralized from barren peraluminous granites.</p>
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1 Nb-Ta fractionation in peraluminous granites: a marker of the
2 magmatic-hydrothermal transition

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14

15 **ABSTRACT**

16 In their late stages of evolution, peraluminous granitic melts exsolve a large amounts of fluids
17 which can modify the chemical composition of granitic whole rocks samples. The Nb/Ta ratio is
18 expected to decrease during magmatic differentiation of granitic melts, but the behavior of both
19 elements at the magmatic-hydrothermal transition remains unclear. Using a compilation of whole
20 rock geochemical data available in the literature, we demonstrate that fractional crystallization
21 alone is not sufficient to explain the distribution of Nb-Ta in most peraluminous granites.

22 However, we notice that most of the granitic samples displaying evidence of interactions with
23 fluid, regardless of their age or their emplacement conditions, have Nb/Ta < 5. We propose that
24 the decrease of the Nb/Ta ratio in highly evolved melts is the consequence of both fractional
25 crystallization and sub-solidus magmatic-hydrothermal alteration. We suggest that the value
26 Nb/Ta = 5 in peraluminous granite fingerprints the magmatic-hydrothermal transition.

27 Furthermore, a Nb/Ta ratio of 5 appears to be a good marker to discriminate mineralized from
28 barren peraluminous granites.

29

30 **INTRODUCTION**

31 In granitic systems, the magmatic-hydrothermal transition separates a purely magmatic system
32 dominated by crystal-melt interaction from a system dominated by crystal-melt-magmatic fluid
33 phase interaction (Halter and Webster, 2014). Hydrothermal activity in peraluminous granites
34 can be either localized, as evidenced by pegmatites and/or quartz veins, or pervasive, leading to
35 significant element mobility and, in the most extreme cases, to the formation of greisens
36 (Pirajno, 2013). Such alteration events occur during the sub-solidus stage of the granitic melt
37 emplacement and may lead to the deposition of economically significant mineralization such as
38 Sn or W.

39 Nb and Ta are lithophile elements considered as “geochemical twins” because they have the
40 same charge and similar ionic radius. As a result they have similar geochemical properties and
41 should not be fractionated during most geological processes (Goldschmidt, 1937). However, in
42 granitic rocks, Nb/Ta ratios are highly variable (< 2 - 25; Green, 1995). Some authors have
43 demonstrated that the Nb/Ta ratios decrease in granites during fractional crystallization
44 (Raimbault et al. 1995; Linnen and Keppler, 1997; Stepanov et al., 2014). Other studies have
45 suggested that Nb and Ta could be fractionated in highly evolved peraluminous granites during
46 the interaction with late magmatic fluids (Dostal and Chatterjee, 2000; Tartèse and Boulvais,
47 2010; Ballouard et al., 2015; Dostal et al., 2015).

48

49 In order to decipher the specific role of the magmatic and hydrothermal processes on the
50 evolution of the Nb/Ta ratios, we compiled whole rock geochemical data available in the
51 literature for peraluminous granites emplaced at different times and in various tectonic contexts.
52 Based on these data, we show that fractional crystallization of granitic melts alone is not
53 sufficient to account for the Nb-Ta behavior observed in most peraluminous granites and that
54 hydrothermal processes are necessarily involved.

55

56 **PRESENT KNOWLEDGE**

57 **Magmatic behavior of Nb-Ta**

58 In highly evolved granites and pegmatites, columbite ((Fe,Mn)Nb₂O₆) and tantalite ((Fe,
59 Mn)Ta₂O₆) are the main mineral phases hosting Nb and Ta. Experimental studies have shown
60 that the solubility of these two minerals in granitic melts increases with temperature, but
61 decreases with increasing the Aluminium Saturation Index (ASI), a parameter related to the
62 degree of polymerization of the melt (Linnen and Keppler, 1997; Aseri et al., 2015). The Li
63 content of granitic melts also increases the solubility of columbite and tantalite (Linnen, 1998;
64 Aseri et al., 2015).

65 Partial melting can produce granitic peraluminous melts with Nb/Ta ratios higher or lower than
66 their source, depending on the temperature. Melts formed during high temperature anatexis tend
67 to have high Nb/Ta ratios, as a result of the complete consumption of biotite and the high
68 abundance of Ti-bearing oxides in the residue, which preferentially incorporate Ta over Nb
69 (Stepanov et al., 2014). Conversely, low temperature partial melting generates melts with low
70 Nb/Ta ratios because residual biotite incorporates preferentially Nb over Ta (Stepanov et al.,
71 2014). Since biotite and Ti-bearing minerals can also be involved during differentiation of

72 granitic melts, fractional crystallization also changes Nb/Ta ratios: Nb/Ta increases during high
73 temperature fractional crystallization of Ti-rich melts due to the preferential saturation of Ti-
74 oxide minerals over biotite, whereas Nb/Ta ratios decrease during low temperature
75 differentiation of granitic melts due to the fractionation of biotite and/or muscovite (Stepanov et
76 al., 2014). In the most evolved peraluminous melts, the lower solubility of manganocolumbite
77 (MnNb_2O_6) compared to manganotantalite (MnTa_2O_6) also enhances the decrease of the Nb/Ta
78 ratio in the melt (Linnen and Keppler, 1997).
79 Melt inclusions in Li-F granites (Orlovka massif, Eastern Transbaikalia) indicate a separation of
80 an immiscible F-rich hydrosaline melt that can induce a decrease of the Nb and Ta contents in
81 the residual melt (Badanina et al., 2010).

82

83 **Nb-Ta behavior in hydrothermal systems**

84 Nb and Ta are poorly soluble in aqueous solutions, Ta being even less soluble than Nb (Zaraisky
85 et al., 2010). Experiments with aqueous F-rich fluids and aluminosilicate melt indicate that Nb
86 and Ta preferentially partition in the melt (Chevychelov et al., 2005). However, the solubility
87 and hydrothermal transfer of Ta and Nb are greatly enhanced in F-rich solutions under reducing
88 conditions (Zaraisky et al., 2010). These experimental results are consistent with the fact that
89 several F-rich cupolas of greisenized peraluminous granites are significantly enriched in both Nb
90 and Ta (e.g. Zaraisky et al., 2009).

91

92 **VARIATIONS OF WHOLE ROCK NB/TA RATIOS IN PERALUMINOUS GRANITES**

93 We compiled data for peraluminous granites (i.e., with a A/CNK ratio > 1) as well as for some
94 greisens of different ages (Archean to Mesozoic) and emplaced in various geodynamical contexts
95 (see Table DR1 in the GSA Data Repository).

96

97 **Nb-Ta fractionation during magmatic processes**

98 In Figure 1, the Nb/Ta ratios are highly variable between ~15 and ~0 when reported as a function
99 of Nb and Ta, the lowest values being recorded by whole rocks displaying the highest Nb and Ta
100 contents. Mica fractionation in granitic melt induces a decrease of the Nb/Ta ratios (Stepanov et
101 al., 2014). In Figure 1, we modeled the evolution of a melt with an initial Ta and Nb contents of
102 1.5 ppm and 12 ppm (Nb/Ta = 8), respectively, undergoing fractionation of a cumulate made of
103 80 wt.% (quartz + feldspar) + 10 wt.% muscovite + 10wt.% biotite, using the Rayleigh
104 distillation law and the silicate-melt partition coefficients compiled by Stepanov et al. (2014).
105 The modeling qualitatively reproduces the behaviors of Nb and Ta, but it requires an unrealistic
106 rate of mineral fractionation (over 90 wt.%) to reach low Nb/Ta ratios around 2 and Nb and Ta
107 contents around 20 and 10 ppm, respectively (Fig. 1). The addition of 0.5 wt.% Fe-Ti oxide
108 (e.g. ilmenite or rutile) in the cumulate, in which Ta and Nb are highly compatibles (Stepanov et
109 al., 2014), makes things even worse. Indeed, the fractionation of this cumulate causes a decrease
110 of the Nb content (Fig. 1A), resulting in a trend opposite to the trend displayed by the
111 peraluminous granites.

112 If crystal-melt fractionation is likely to occur during the crystallization of granitic melts in
113 magmatic bodies (Dufek and Bachmann, 2010) and during the magma ascent in dykes (Tartèse
114 and Boulvais, 2010; Yamato et al., 2012), numerical modeling shows that the efficiency of
115 crystal-melt segregation is restricted to cases where crystals represent a low percentage of the

116 total magma volume (Yamato et al., in press). Indeed, 70-75% of crystallization marks the
117 particle locking threshold (PLT in Figure 1B, Vigneresse et al., 1996) where the liquid becomes
118 totally locked, precluding any crystal-melt segregation. The model presented here thus suggests
119 that fractional crystallization alone is not sufficient to explain the behaviors of Nb and Ta in
120 peraluminous granitic rocks.

121

122 **Nb-Ta fractionation during magmatic-hydrothermal processes**

123 *Mineralogical markers*

124 Secondary muscovitization and greisenization occur under sub-solidus conditions during the
125 interaction between crystallized granites and acidic late magmatic fluids (Pirajno, 2013). The
126 Figure 2 shows that the Nb/Ta ratios of whole rock granites and greisens are anti-correlated with
127 the average $\text{MgO}/(\text{Na}_2\text{O} + \text{TiO}_2)$ ratios of the muscovite they host (a chemical marker for
128 secondary muscovitization, Miller et al., 1981). This observed anti-correlation suggests that the
129 fluids involved in the secondary muscovitization processes could also be responsible for the
130 decrease of the Nb/Ta whole-rock values. Whole rock hydrothermal enrichment of Ta during
131 secondary muscovitization is, for example, observed in ongonites (topaz-bearing
132 microleucogranites) from the Ongon Kairkhan (Mongolia) and this process is associated with the
133 crystallization of late Ta-rich overgrowth on Nb-Ta oxides (Dostal et al., 2015).

134

135 *Geochemical markers*

136 The whole rock Nb/Ta ratios of peraluminous granites are anti-correlated with their Sn contents,
137 an element highly mobilized at the magmatic-hydrothermal transition (Fig. 3A): high Sn contents
138 above ~30 ppm are only encountered in granitic samples (or greisens) with low Nb/Ta (< 5).

139 These samples also display high contents in Cs, F, Li, W and Rb. Because such incompatible
140 elements present a strong affinity for magmatic fluids, their enrichment is commonly used as a
141 marker of a magmatic-hydrothermal alteration in highly evolved crustal granites. Indeed,
142 increasing the abundance of highly incompatible elements, with a bulk partition coefficient K_d
143 between the mineral phases and the melt close to 0, by two orders of magnitude, as observed in
144 Figure 3A (from ~10 to ~1000 ppm), during fractional crystallization requires a unrealistic
145 degree of fractional crystallization up to 99 wt.%, suggesting that hydrothermal processes are
146 also involved. Such enrichments in highly incompatible element, attributed to interaction with
147 magmatic fluids, have been noticed in the Erzgebirge massif (Förster et al., 1999), in the South
148 Mountain Batholith (e.g. Dostal and Chatterjee, 2000), or in the French Armorican Massif
149 (Tartèse and Boulvais, 2010; Ballouard et al., 2015).

150

151 The Nb/Ta ratios also correlate with the K/Rb ratios (Fig. 3B). Most granites with low Nb/Ta
152 display K/Rb values lower than 150, characteristic of the pegmatite-hydrothermal evolution
153 (Shaw, 1968). Such a tendency is observed in the South Mountain Batholith, where it was
154 interpreted as evidence for a magmatic-hydrothermal alteration (Dostal and Chatterjee, 2000).

155

156 Finally, the whole rock Nb/Ta ratios can be compared with the magnitude of the tetrad effect,
157 which corresponds to the intra-REE fractionation observed in the REE patterns of highly
158 fractionated magmatic rocks and hydrothermal precipitates (e.g. Irber, 1999). Although Duc-Tin
159 and Kepller (2015) have recently suggested that the tetrad effect could result from monazite and
160 xenotime fractionation, most authors have argued that such REE patterns actually reflect a
161 selective complexation of the REE during the interaction of granitic melts with F- and Cl-rich

162 aqueous fluids (e.g. Bau, 1996; Irber, 1999; Monecke et al., 2007). Irber (1999) quantified the
163 degree of tetrad effect (TE_{1-3}) by determining the deviation of the first and the third tetrad of
164 granites REE-patterns from a hypothetical tetrad effect-free REE pattern. The large majority of
165 the samples with significant tetrad effect ($TE_{1-3} > 1.1$) are also characterized by low Nb/Ta ratios
166 below ~5 (Fig.3C).

167

168 *Metallogenic markers*

169 The Nb/Ta ratio is commonly compared to the Zr/Hf ratio, as the latter has been proposed as
170 either a marker of magmatic-hydrothermal interactions (Bau, 1996) or of fractional
171 crystallization (Linnen and Keppler, 2002; Claiborne et al., 2006). The Zr/Hf ratio is a
172 geochemical indicator of the fertility of granitic rocks as a Zr/Hf ratios below ~25
173 (corresponding to the lower limit of the CHARGE and RADIUS Control range; Bau, 1996) are
174 expected in granites where Sn, W, Mo, Be and Ta mineralization are described (Zaraisky et al.,
175 2009). In a Nb/Ta vs. Zr/Hf diagram (Fig. 4), most barren granites plot in the field defined by
176 $< Zr/Hf < 46$ (CHARAC range of Bau, 1996) and by $5 < Nb/Ta < 16$, whereas peraluminous
177 granites associated with Sn, W and/or U deposits have $18 < Zr/Hf < 46$ with Nb/Ta ratio lower
178 than 5. Rare metals granites are characterized by even lower Zr/Hf ratios (< 18) with Nb/Ta
179 ratios that are still lower than 5.

180

181 From the diagrams presented in Figures 2, 3 and 4, we highlight significant mineralogical
182 (secondary muscovitization), geochemical (Sn contents, K/Rb ratio, tetrad effect) and
183 metallogenic (Sn-W-U and rare metal mineralization) evidence that magmatic-hydrothermal
184 processes account for the decrease of the Nb/Ta ratio in peraluminous granites. The solubility

185 and hydrothermal transfer of Nb and Ta are greatly enhanced, by up to three orders of
186 magnitude, in reduced F-rich aqueous solutions (Zaraisky et al., 2010). Therefore, in
187 peraluminous granites affected by sub-solidus alteration, the Nb/Ta ratios can be lowered by an
188 increase of the Ta content in Ta-Nb-bearing minerals due to the lower mobility of Ta compared
189 to Nb in aqueous solutions. As a consequence, we suggest here that the decrease of the Nb/Ta
190 ratios to values lower than ~5 in peraluminous granites reflects the concomitant effect of
191 fractional crystallization and sub-solidus magmatic-hydrothermal alteration, likely by F-rich
192 acidic reduced fluids of magmatic origin.

193

194 **Nb/Ta = 5: a critical ratio for granite petrogenesis and mineral exploration strategies**

195 The peraluminous granite whole rock samples with Nb/Ta ratios lower than 5 show significant
196 evidence of interaction with fluids. We suggest that Nb/Ta = 5 represents a threshold between a
197 purely magmatic system (Nb/Ta > 5) and a magmatic-hydrothermal system (Nb/Ta < 5). Taking
198 a cut off value of 5 for the Nb/Ta ratio as a marker of the magmatic-hydrothermal transition in
199 peraluminous granites bears some implications for exploration strategies as it can also help to
200 define the economic potential of these granites. Indeed, Figure 4 demonstrates that a Nb/Ta ratio
201 of 5 can be used as a geochemical indicator to differentiate barren granites from granites
202 spatially related to Sn-W-(U) or rare metals mineralization. Since whole rock trace element
203 analyses (including Nb and Ta) are routinely performed in most laboratories around the world,
204 the simple calculation of whole rock sample Nb/Ta ratios can, therefore, help exploration
205 geologists to define potential targets for Sn-W-(U) and rare metals deposits.

206

207 **CONCLUSION**

208 The mineralogical and geochemical evidence of fluid interaction recorded in granitic whole rock
209 samples, indicate that the value $Nb/Ta = 5$ is a good marker of the magmatic-hydrothermal
210 transition in peraluminous granites. The decrease of the Nb/Ta ratio in peraluminous granites is
211 associated with an increase of the degree of secondary muscovitization and with geochemical
212 and metallogenic evidence of hydrothermal interactions, suggesting that sub-solidus alteration is
213 involved in the fractionation of Nb-Ta. To further constrain the mechanisms involved in the
214 fractionation of Nb/Ta ratios in peraluminous granites at the magmatic-hydrothermal transition,
215 mineral-scale analyses would now be required. From an exploration point of view, and based on
216 the large compilation of data presented in this study, the Nb/Ta ratio appears to be a good
217 geochemical indicator to differentiate barren from ore-bearing peraluminous granites.

218

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222

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326 **FIGURE CAPTIONS**

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329 Figure 1. Nb/Ta vs. (A) Nb and (B) Ta abundances for peraluminous granites. The colored curves
330 represent a model of evolution of Nb and Ta in a liquid L_0 (Nb= 12 ppm, Ta =1.5 ppm, Nb/Ta =
331 8) during the fractionation of an assemblage made of 10 wt.% biotite + 10 wt.% muscovite + 80
332 wt.% (quartz + feldspar). The numbers above the curves indicate the amount of fractional
333 crystallization. The black dashed line represents the same model during the fractionation of an
334 assemblage composed of 10 wt.% biotite + 10 wt.% muscovite + 0.5 wt.% ilmenite + 79.5 wt.%
335 (quartz + feldspar). The K_d used and presented in the table in inset in the diagram are from
336 Stepanov et al. (2014) and reference therein. PLT: Particle Locking Threshold (Vigneresse et al.,
337 1996).

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340 Figure 2. (A) Mg-Na-Ti ternary classification diagram of muscovite (Miller et al., 1981). (B)
341 Diagram reporting the evolution of Nb/Ta ratios for whole rock samples from different
342 peraluminous granites against the average value of the $MgO/(Na_2O + TiO_2)$ ratios of their
343 dioctahedral micas.

344

345

346 Figure 3: Evolution of Nb/Ta ratios of peraluminous granites as a function of selected markers of
347 magmatic-hydrothermal alteration. The degree of tetrad effect (TE_{1-3}) has been calculated using
348 the equation of Irber (1999). CC: Continental Crust composition (from Rudnick and Gao, 2005).

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351 Figure 4. Nb/Ta vs. Zr/Hf diagram differentiating barren and ore-bearing peraluminous granites.

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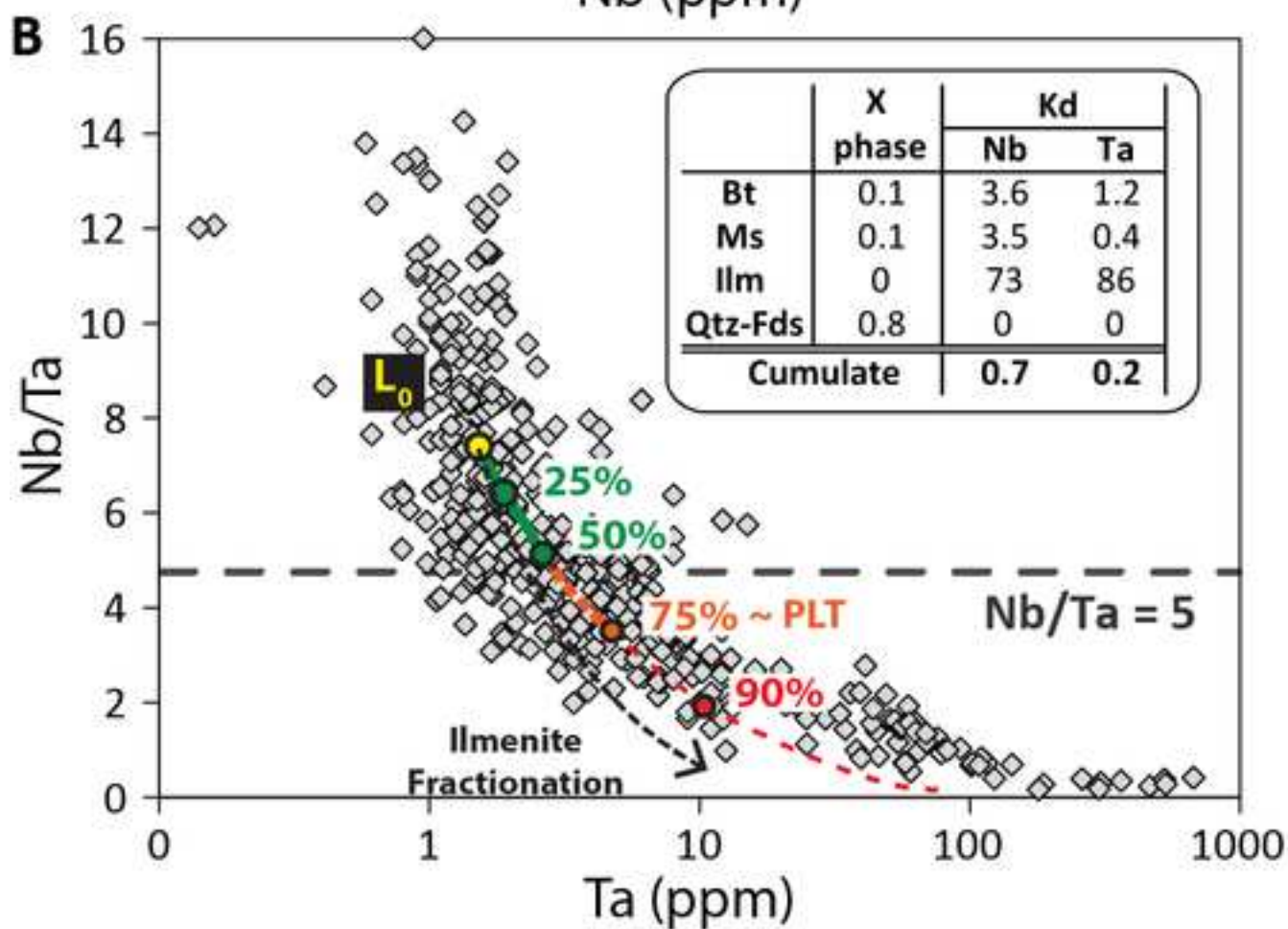
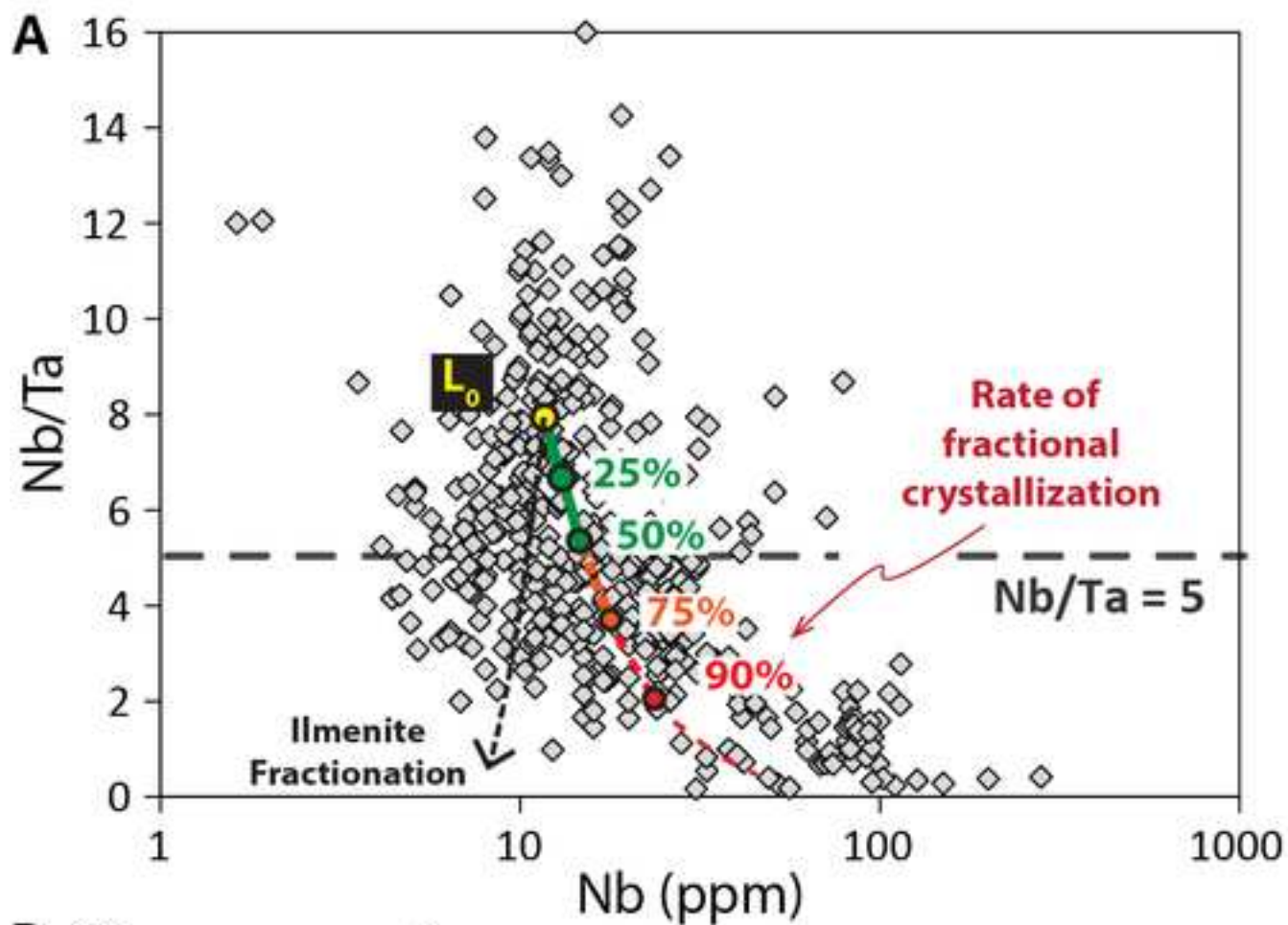
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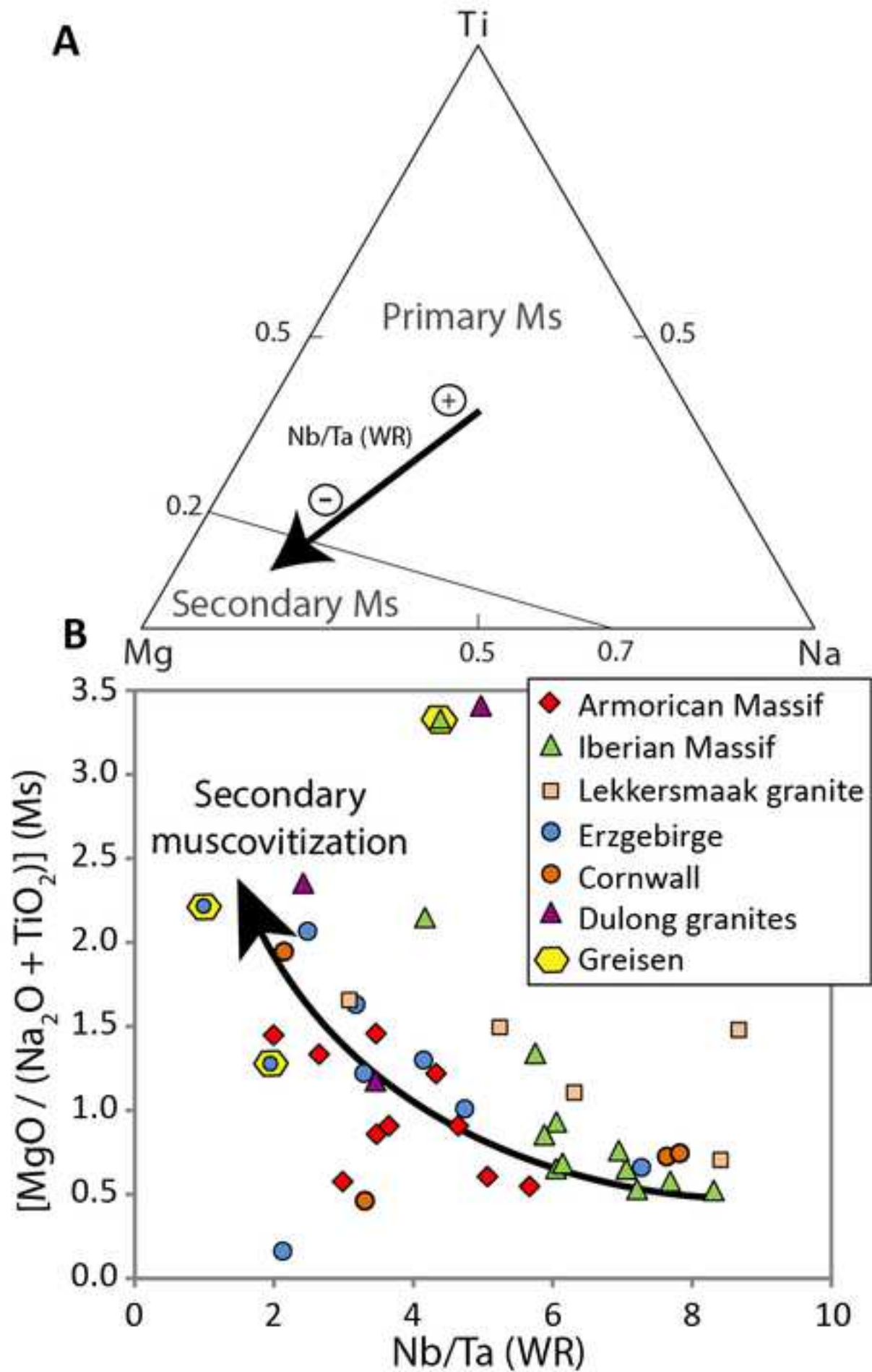
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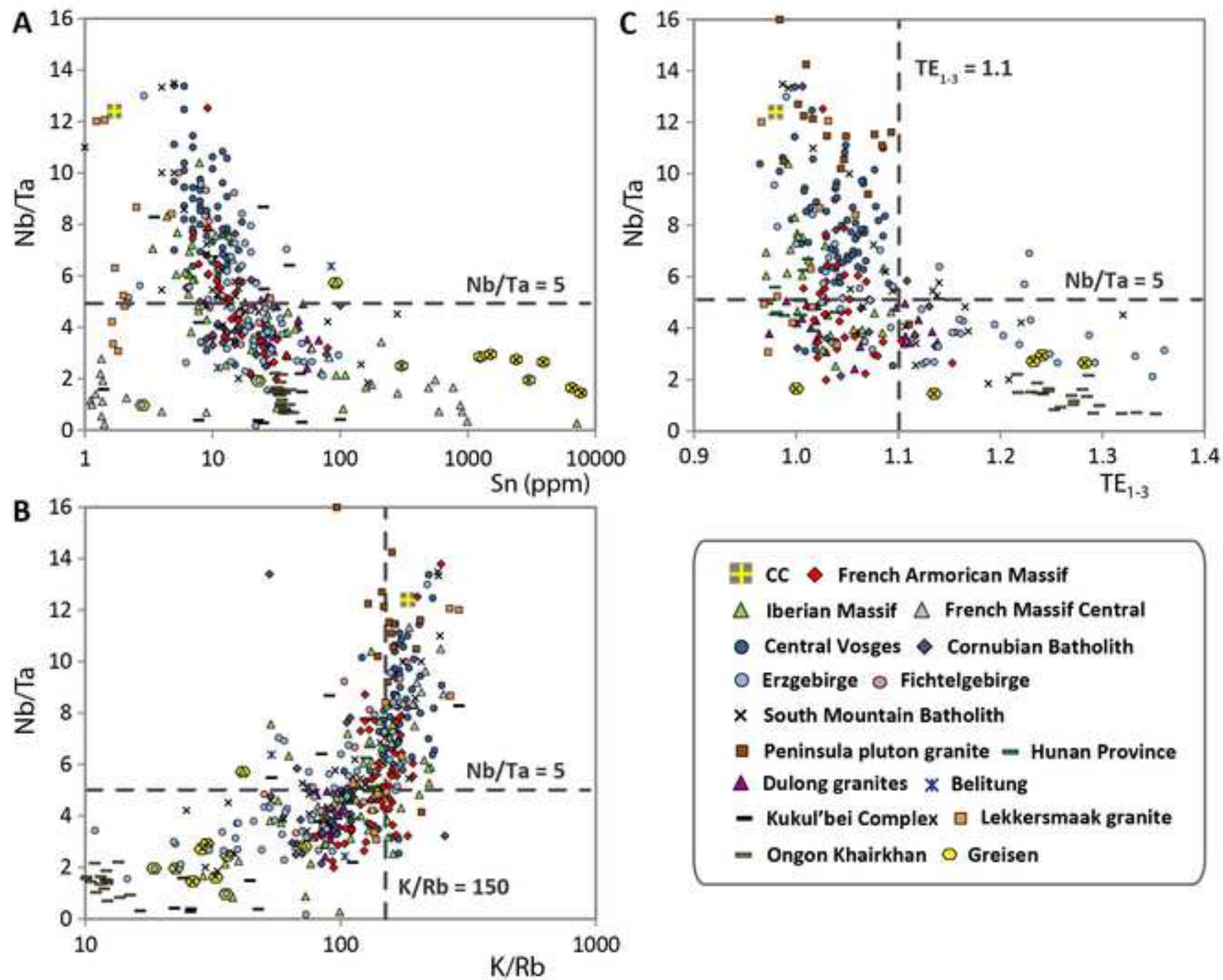
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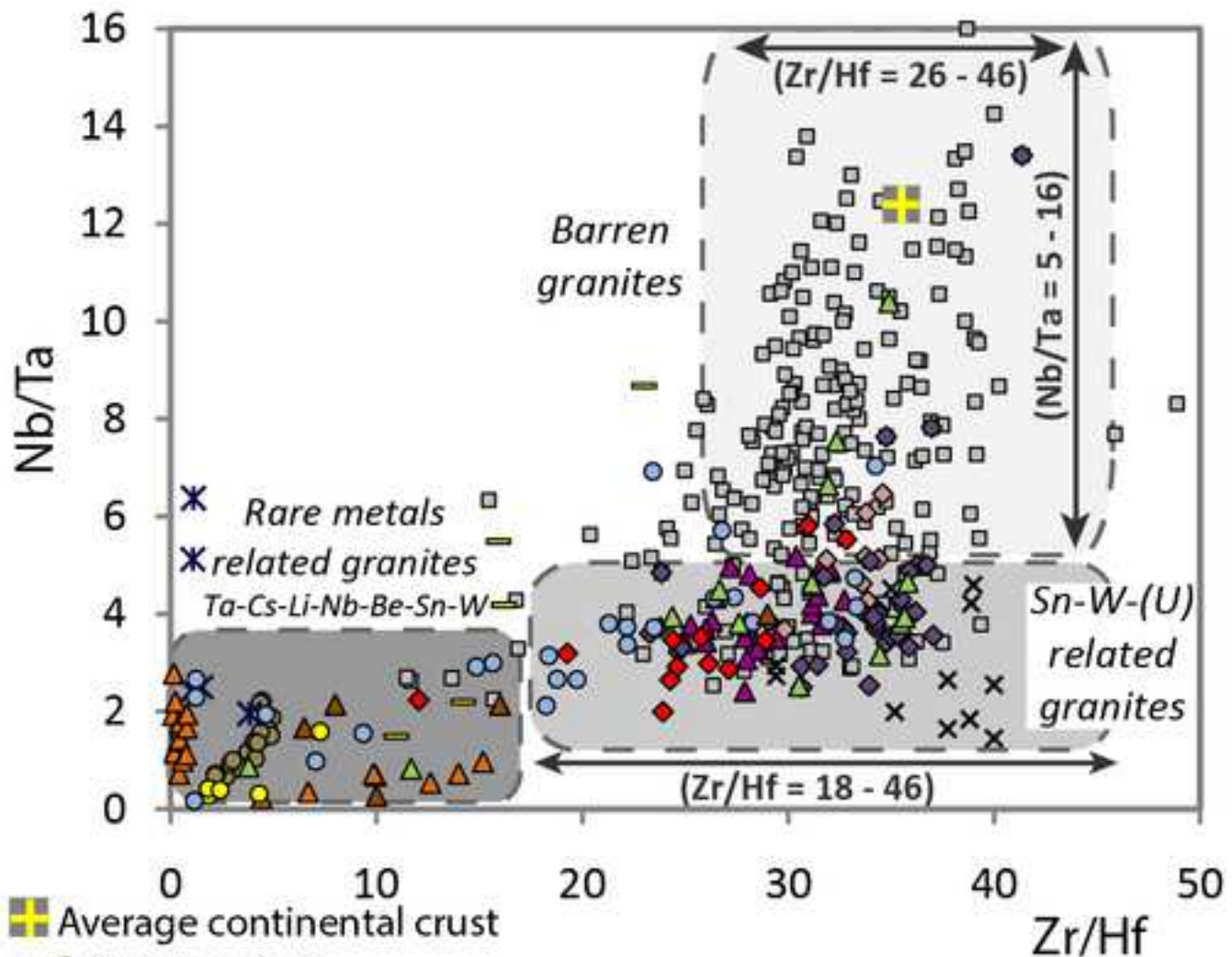
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357 ¹GSA Data Repository item 2015xxx, [[Synthesis of peraluminous crustal granites reported in](#)
358 [this study](#)], is available online at www.geosociety.org/pubs/ft2015.htm, or on request from
359 editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301,
360 USA.









- ✚ Average continental crust
- Barren granites
- ◇ Lizio granite - Armorican Massif : **Sn**
- ◆ Questembert and Guérande granites - Armorican Massif : **U - (Sn)**
- ▲ Beariz, Jalama and Carbalinno granites - Iberian Massif : **Sn - W - (Nb - Ta)**
- ◆ Cornubian batholith : **Sn - W - (Cu)**
- Li - mica granites and greisens from the Erzgebirge : **Sn - W**
- × Leucogranites and greisens from the Davis Lake pluton - SMB : **Sn**
- ✚ Tanjungpandan pluton - Belitung - Indonesia: **Sn-W**
- Leucogranites from the Kukul'bei Complex - Transbaikalia: **W - Sn**
- ▲ Dulong granites - Yunnan Province - South China: **Sn**
- Ongonites from Ongon Kairkhan, Central Mongolia : **W**
- Li - F granites from the Kukul'bei Complex - Transbaikalia : **Ta**
- ▲ Beauvoir granite - Massif Central: **Ta - Be - Sn - Li**
- ▲ Ponte Segade granite - Iberian Massif : **Sn - Ta - Nb - Li - Be - Cs**

Location	Igneous province	Granite	Age	Related deposit	Reference	
Western Europe	French Armorican Massif	Lizio	ca. 316 Ma	Sn	U leached during hydrothermal alteration Apical zone facies	Tartèse and Boulvais, 2010 Tartèse and Boulvais, 2010; Tartèse et al., 2013 Ballouard et al., 2015 Georget, 1986 Georget, 1986
		Questembert	ca. 316 Ma	(U)		
		Guérande	ca. 310 Ma	U - Sn		
		Huelgat	Late Carboniferous	-		
	Iberian massif	Brignogan	Late Carboniferous	-		
		Ponte Segade	Late Carboniferous	Sn - Ta - Nb - Li - Be - Cs	Canosa et al., 2012 Ramírez and Grundvig, 2000 Gloaguen, 2006 Gloaguen, 2006 Gloaguen, 2006 Gloaguen, 2006 Gloaguen, 2006 Bea et al., 1994 Nieva, 2002 Nieva, 2002	
		Jalama	Late Carboniferous	Sn-W-(Nb-Ta)		
		Beariz (Avion)	Late Carboniferous	-		
Beariz		Late Carboniferous	Sn -W			
Boboraz		Late Carboniferous	-			
Carballino		Late Carboniferous	Sn-W-(Nb-Ta)			
Irixo	Late Carboniferous	-				
Pedrobernardo	c.a. 300 Ma	-				
S. Mamede de Ribatua	Hercynian	Sn-W				
Panasqueira	Hercynian	Sn-W				
French Massif Central	Colette	ca. 310 Ma	-	Ta - Be -Sn - Li	Raimbault et al., 1995 Raimbault et al., 1995 Rolin et al., 2006	
	Beauvoir	ca. 310 Ma				
Guéret	ca. 350 Ma	-				
Cornubian Batholith	-	295-275 Ma	Sn - W - (Cu)	Chappell and Hine, 2006; Müller et al., 2006		
Erzgebirge	-	Late Carboniferous - Early Permian	Sn - U -W	Li - mica granites and greisens	Förster et al., 1999; Breiter, 2012; Štemprok et al., 2005	
Fichtelgebirge	-	Late Carboniferous - Early Permian	?		Hecht et al., 1997	
Central Vosges	-	329 - 322 Ma	-		Tabaud et al., 2015	
Nova Scotia - Canada	South Mountain Batholith	-	Late Devonian	-	MacDonald et al., 1992	
		Davis Lake	Late Devonian	Sn	Topaz muscovite leucogranites and greisens	Dostal and Chatterjee, 1995
South Africa	Kaapvaal Craton	Lekkersmaak granite suite	ca. 2800 Ma	-	Jaguin, 2012	
	Cape Granite Suite	Peninsula pluton	556-534 Ma	-	Farina et al., 2012	
South China	Hunan Province	Indosinian granites	210 – 243 Ma	?	Wang et al., 2007	
	Yunnan Province	Dulong granites	ca. 90 Ma	Sn	Xu et al., 2015	
Indonesia	Belitung	Tanjungpandan pluton	ca. 215 Ma	Sn - W	Schwartz and Surjono, 1990	
Eastern Transbaikalia	-	Kukul'bei complex	ca. 140 Ma	W – Sn Ta	Muscovite leucogranites (phase 2) Albite-amazonite Li-F granites (phase 3)	Zaraisky et al., 2009
Central Mongolia	-	Ongon Khairkhan	Ca. 120 Ma	W	Ongonites (topaz bearing albite-rich microleucogranites)	Dostal et al., 2015

Table DR1: Synthesis of the peraluminous granites reported in this study with their location, their age, their associated metal deposits when available and the corresponding references.

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