

Nb-Ta fractionation in peraluminous granites: A marker of the magmatic-hydrothermal transition

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

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Abstract:	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.				
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1 Nb-Ta fractionation in peraluminous granites: a marker of the

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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 fluid, regardless of their age or their emplacement conditions, have Nb/Ta < 5. We propose that 23 24 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 25 Nb/Ta = 5 in peraluminous granite fingerprints the magmatic-hydrothermal transition. 26

Furthermore, a Nb/Ta ratio of 5 appears to be a good marker to discriminate mineralized from
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 emplacement and may lead to the deposition of economically significant mineralization such as 37 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,

2010; Ballouard et al., 2015; Dostal et al., 2015).

48

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

55

56 **PRESENT KNOWLEDGE**

57 Magmatic behavior of Nb-Ta

In highly evolved granites and pegmatites, columbite ((Fe,Mn)Nb₂O₆) and tantalite ((Fe,
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).

Partial melting can produce granitic peraluminous melts with Nb/Ta ratios higher or lower than their source, depending on the temperature. Melts formed during high temperature anatexis tend to have high Nb/Ta ratios, as a result of the complete consumption of biotite and the high abundance of Ti-bearing oxides in the residue, which preferentially incorporate Ta over Nb (Stepanov et al., 2014). Conversely, low temperature partial melting generates melts with low Nb/Ta ratios because residual biotite incorporates preferentially Nb over Ta (Stepanov et al., 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 (MnNb₂O₆) compared to manganotantalite (MnTa₂O₆) 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

We compiled data for peraluminous granites (i.e., with a A/CNK ratio > 1) as well as for some
greisens of different ages (Archean to Mesozoic) and emplaced in various geodynamical contexts
(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

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 MgO/(Na ₂ O + 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 Kd 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

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

Finally, the whole rock Nb/Ta ratios can be compared with the magnitude of the tetrad effect, which corresponds to the intra-REE fractionation observed in the REE patterns of highly fractionated magmatic rocks and hydrothermal precipitates (e.g. Irber, 1999). Although Duc-Tin and Kepller (2015) have recently suggested that the tetrad effect could result from monazite and xenotime fractionation, most authors have argued that such REE patterns actually reflect a 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 26

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

From the diagrams presented in Figures 2, 3 and 4, we highlight significant mineralogical (secondary muscovitization), geochemical (Sn contents, K/Rb ratio, tetrad effect) and metallogenic (Sn-W-U and rare metal mineralization) evidence that magmatic-hydrothermal 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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Figure 1.Nb/Ta vs. (A) Nb and (B) Ta abundances for peraluminous granites. The colored curves represent a model of evolution of Nb and Ta in a liquid L_0 (Nb= 12 ppm, Ta = 1.5 ppm, Nb/Ta = 8) during the fractionation of an assemblage made of 10 wt.% biotite + 10 wt.% muscovite + 80 wt.% (quartz + feldspar). The numbers above the curves indicate the amount of fractional crystallization. The black dashed line represents the same model during the fractionation of an assemblage composed of 10 wt.% biotite + 10 wt.% muscovite + 0.5 wt.% ilmenite + 79.5 wt.% (quartz + feldspar). The Kd used and presented in the table in inset in the diagram are from Stepanov et al. (2014) and reference therein. PLT: Particle Locking Threshold (Vigneresse et al., 1996). Figure 2. (A) Mg-Na-Ti ternary classification diagram of muscovite (Miller et al., 1981). (B) Diagram reporting the evolution of Nb/Ta ratios for whole rock samples from different peraluminous granites against the average value of the $MgO/(Na_2O + TiO_2)$ ratios of their diochtaedral micas. Figure 3: Evolution of Nb/Ta ratios of peraluminous granites as a function of selected markers of magmatic-hydrothermal alteration. The degree of tetrad effect (TE_{1-3}) has been calculated using the equation of Irber (1999). CC: Continental Crust composition (from Rudnick and Gao, 2005). Figure 4.Nb/Ta vs.Zr/Hf diagram differentiating barren and ore-bearing peraluminous granites.

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











- 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
- **x** 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
- A Beauvoir granite Massif Central: Ta Be Sn Li
- Ponte Segade granite Iberian Massif : Sn Ta Nb Li Be Cs

Location	lgneous province	Granite	Age		Related deposit	Reference
		Lizio	ca. 316 Ma	Sn		Tartèse and Boulvais, 2010
	French	Questembert	ca. 316 Ma	(11)	U leached during hydrothermal alteration	Tartèse and Boulvais, 2010;
	Armorican	Questembert		(8)	o leachea aanng nyarothermaratteration	Tartèse et al., 2013
	Massif	Guérande	ca. 310 Ma	U - Sn	Apical zone facies	Ballouard et al., 2015
	ivid Soli	Huelgat	Late Carboniferous	-		Georget, 1986
		Brignogan	Late Carboniferous	-		Georget, 1986
		Ponte Segade	Late Carboniferous	Sn - Ta - Nb -Li -Be -Cs		Canosa et al., 2012
		Jalama	Late Carboniferous	Sn-W-(Nb-Ta)		Ramírez and Grundvig, 2000
		Beariz (Avion)	Late Carboniferous	-		Gloaguen, 2006
		Beariz	Late Carboniferous	Sn -W		Gloaguen, 2006
	Iberian massif	Boboraz	Late Carboniferous	-		Gloaguen, 2006
		Carballino	Late Carboniferous	Sn-W-(Nb-Ta)		Gloaguen, 2006
Western		Irixo	Late Carboniferous	-		Gloaguen, 2006
Europe		Pedrobernardo	c.a. 300 Ma	-		Bea et al., 1994
		S. Mamede de Ribatua	Hercynian	Sn-W		Nieva, 2002
		Panasqueira	Hercynian	Sn-W		Nieva, 2002
	French Massif	Colette	ca. 310 Ma	-		Raimbault et al., 1995
	Central	Beauvoir	ca. 310 Ma	Ta - Be -Sn - Li		Raimbault et al., 1995
		Guéret	ca. 350 Ma	-		Rolin et al., 2006
	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,
	Fichtelgehirge	_	Late Carboniferous - Farly Permian	2		Hecht et al. 1997
	- tentengebinge			· ·		
	Central Vosges	-	329 - 322 Ma	-		Tabaud et al., 2015
Nova Scotia -	South	-	Late Devonian	-		MacDonald et al., 1992
Canada	Batholith	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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